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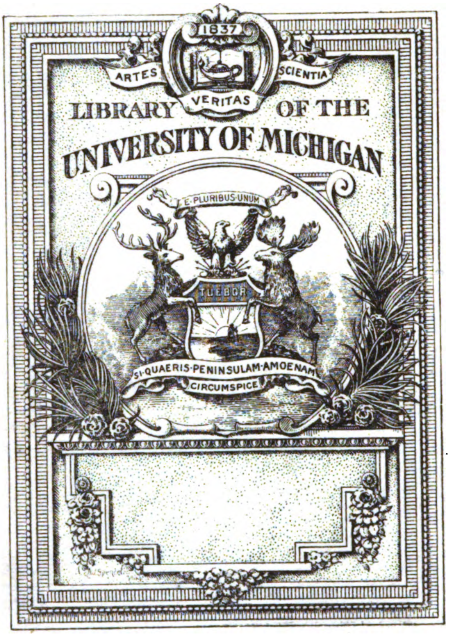
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CHEMICAL ANALYSIS.

PART II. QUANTITATIVE.

A MANUAL

OF

CHEMICAL ANALYSIS,

QUALITATIVE AND QUANTITATIVE.

FOR THE USE OF STUDENTS.

PART II.
QUANTITATIVE.

BY

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MANUAL

OF

CHEMICAL ANALYSIS.

PART II.

QUANTITATIVE.

CHAPTER VII.

ON QUANTITATIVE OPERATIONS.

1. WEIGHING.

145. *The Balance.*—Of the various implements required by the analytical chemist in the prosecution of his labours, the *balance* is perhaps the most important; for of what value would the most elaborate and exact experiment be, without a means of ascertaining the quantitative result? The *balance* therefore demands our first attention.

The process of weighing may be performed in a variety of ways, and with various kinds of machines; but the instrument invariably employed by the chemist for determining the weights of the substances on which he is engaged, is what is generally known as the common balance, which is a lever of the first kind, with equal arms. A detailed investigation of the circumstances which regulate the sensibility of a balance, and a mathematical development of the principles on which it is constructed, would be out of place here: it may not, however, be amiss to describe briefly some of the most important points connected with its construction and properties.

The philosophical balance may be described as a uniform inflexible lever or beam, Fig. 41, made as light as is consistent

with a proper degree of strength, and having three axes, one, the *fulcrum*, or centre of motion, C, on which it turns, and the other two, A and B, situated at equal distances from the fulcrum near to the extremities of the beam, and from which the scales

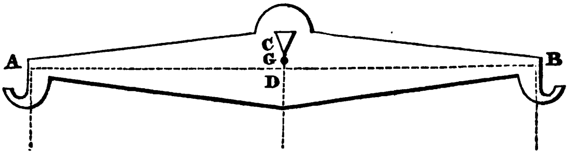


Fig. 41.

or pans depend: the beam thus supports the scales, and is itself supported by means of fine edges of hard steel working on steel, agate, or garnet, in order that the motion may be free and the distances of the points precisely defined. The scales hanging from fixed points in the beam, act on them always in the direction of gravity; and the effect is the same as if the whole weight were concentrated in those points.

The requisites for a good balance are:—

(1) That the centre of gravity, G, shall be immediately below the fulcrum or centre of motion, C.

(2) That the fulcrum or centre of motion shall be in the same right line with the points of suspension of the scales; so that a straight line drawn from one extremity of the beam to the other, shall be exactly perpendicular to the straight line, C D, joining the centre of gravity with the centre of motion; and

(3) That the arms shall be of equal length.

For if, in the first place, the centre of gravity and the centre of motion be coincident, the beam will rest in any indifferent position, the scales being equally loaded; but if the centre of gravity be above the centre of motion, then the slightest impulse will cause the beam to upset: if, however, the centre of gravity be immediately under the fulcrum, then the line joining it with the latter will always settle itself so as to be in a vertical direction; this line has the properties of a pendulum, the shorter it is, the greater the angle formed by its vibration from a given impulse, consequently the nearer the centre of gravity to the centre of motion, the greater the effect of a given weight added to the scale; or, in other words, the more delicate the balance. The nearer also the centre of gravity of a balance is to its

fulcrum, the slower will be the oscillations of the beam. The number of oscillations, therefore, made by the beam in a given time, affords the most accurate method of judging of the sensibility of the instrument, which will be the *greater* as the oscillations are *fewer*.

In the second place, if the points of suspension of the pans be situated below the centre of motion of the beam, the effect of each addition of weight to the scales will be to *lower* more and more the centre of gravity; and this we have just seen diminishes the sensibility of the balance. If, on the other hand, the points of suspension of the pans are *above* the fulcrum, the effect of the addition of weights will be to *raise* the centre of gravity, thus increasing the sensibility of the instrument (*cæteris paribus*), until at length the centre of gravity becomes itself the centre of motion, when the beam will rest indifferently in any position; and finally, by a further addition of weights, the centre of gravity becomes raised above the fulcrum, and the balance upsets from the smallest disturbance.

In the third place, with respect to the equality of the arms, this condition is of course essential to a good balance; it is nevertheless possible to weigh as accurately with a balance with unequal arms as with one of the same workmanship with equal arms; for this purpose the substance to be weighed is put into either scale and counterpoised by sand, shot, or any other material, with the greatest accuracy; the substance is then removed and the balance once more brought into a state of equilibrium by substituting weights, which, it is perfectly obvious, must, under these circumstances, absolutely represent the weight of the substance under examination. It is not unfrequent to meet with commercial balances constructed with unequal arms for fraudulent purposes, the substance to be sold being always put into the scale depending from the longer arm; the fraud is detected by simply transposing the substance and the weights after equilibrium has been established between them.

Sensibility and *stability* are two properties essential to a good balance.

The *sensibility* of a balance is estimated by observing the angle through which a very small weight inclines the beam; thus supposing we wish to compare the sensibility of two balances, and that a grain weight put into a scale of each inclines the beam of the first 4°, and that of the second only 2°, then the first is twice as sensible as the second. Now, as the

force which acts in turning the beam is proportional to the weight multiplied into the length of the lever at the extremity of which it acts, it is evident that, for a given weight, the sensibility of the balance (*cæteris paribus*) is proportional to the length of the beam.

The *stability* of a balance is the force with which the beam endeavours to recover its equilibrium, and oscillate about its position of rest after it has been disturbed. This force is made up of two parts, the first of which is proportional to the weight of the *beam* multiplied into the length of the lever on which it acts (C G, Fig. 41); and the second is proportional to the *load* multiplied into its length of lever; the whole restoring force then, and that which the predominating weight has to overcome in turning the scale, is proportional to the weight of the beam multiplied into the length of the lever on which it acts, added to the load multiplied into its length of lever. It is evident, then, that *sensibility* and *stability* are two properties in some degree opposed to each other, and that whatever tends to increase the one diminishes the other. The best construction is to make the lever through which the load acts equal to nothing, and this is done by placing the three points of action, A B C, Fig. 41, in the same straight line as has already been explained, and by keeping the centre of gravity a little below that line: the sensibility of the balance is thus rendered independent of the load, and this important property is still further increased by making the beam as light as possible.

The conditions of a perfect balance, as determined by theory, are the guides to the artist in the construction of a good instrument; and although an absolutely perfect balance is practically unattainable, nevertheless, by attending carefully to the principles above explained, the sensibility may be carried to a surprising extent. There is, in the possession of the Royal Society, a balance made by Ramsden, which is capable of weighing ten pounds, and is said to turn with the ten-millionth part of that load, or the thousandth part of a grain. The balances constructed by the late Mr. Robinson have long enjoyed a just celebrity. They are thus described by Captain Kater ('*Lardner's Cyclopædia,*' *Treatise on Mechanics*), who himself constructed an instrument for verifying the national standard bushel, which is probably the most sensible that has yet been made (*Phil. Trans.* 1826). "The beam of Robinson's balance is only 10 inches long. It is a frame of bell-metal, in the

form of a *rhombus*. The fulcrum is an equilateral triangular prism of steel, 1 inch in length; but the edge on which the beam vibrates is formed to an angle of 120°, in order to prevent any injury from the weight with which it may be loaded. The chief peculiarity in this balance consists in the knife-edge which forms the fulcrum bearing upon an agate plane throughout its whole length. The supports for the scales are knife-edges, each $\frac{5}{10}$ths of an inch long. These are furnished each with two pressing-screws, by means of which they may be made parallel to the central knife-edge. Each edge of the beam is sprung obliquely upwards and towards the middle, so as to form a spring, through which a pushing screw passes, and serves to vary the distance of the point of support from the fulcrum, and at the same time, by its oblique action, to raise or depress it, so as to furnish a means of bringing the points of support and the fulcrum into a right line. A piece of wire, 4 inches long, on which a screw is cut, proceeds from the middle of the beam downwards. This is pointed to serve as an index, and a small brass ball moves on the screw, by changing the situation of which the place of the centre of gravity may be varied at pleasure. The fulcrum, as before remarked, rests upon an agate plane throughout its whole length, and the scale-pans are attached to planes of agate which rest upon the knife-edges, forming the points of support. This method of supporting the scale-pans is believed to be due to Mr. Cavendish. Upon the lower half of the pillar, to which the agate plane is fixed, a tube slides up and down by means of a lever which passes to the outside of the case. From the top of this tube arms proceed obliquely towards the ends of the balance, serving to support a horizontal piece, carrying at each extremity two sets of Y's, one a little above the other. The upper Y's are destined to receive agate planes, to which the scale-pans are attached, and thus to relieve the knife-edges from their pressure; the lower to receive the knife-edges which form the points of support: consequently these latter Y's, when in action, sustain the whole beam.

"When the lever is freed from a notch in which it is lodged, a spring is allowed to act upon the tube we have mentioned, and to elevate it. The upper Y's first meet the agate planes carrying the scale-pans and free them from the knife-edge. The lower Y's then come into action and raise the whole beam, elevating the central knife-edge above the agate plane. This is

the usual state of the balance when not in use; when it is brought into action the reverse of what we have described takes place. On pressing down the lever, the central knife-edge first meets the agate plane, and afterwards the two agate planes carrying the scale-pans are deposited upon their supporting knife-edges."

A balance of this kind was employed by Captain Kater in adjusting the national standard pound. With a pound troy in each scale, the addition of $\frac{1}{100}$th of a grain caused the index to vary one division, equal to $\frac{1}{10}$th of an inch; and Mr. Robinson adjusted these balances so that, with 1000 grains in each scale, the index varied perceptibly on the addition of $\frac{1}{1000}$ of a grain, or of one-millionth part of the weight to be determined.

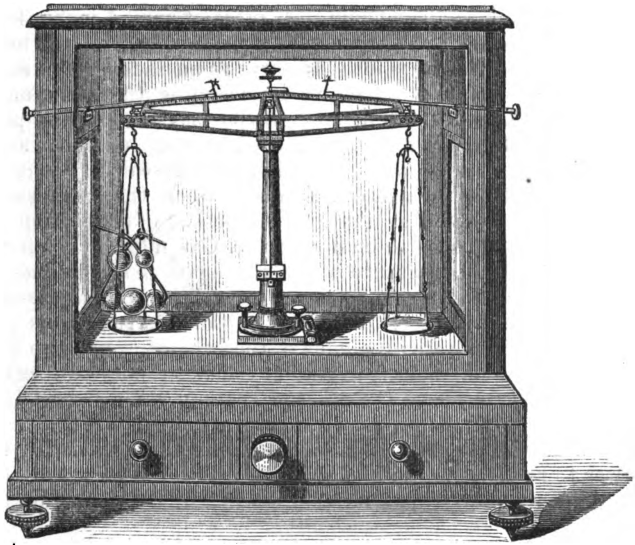


Fig. 42.

Fig. 42 represents a useful chemical balance, constructed by Messrs. Ladd and Oertling, of Moorgate Street, London, intended to carry from 700 to 1000 grains, which will, when loaded, indicate the $\frac{1}{100}$th of a grain. It is represented in the

figure with a Liebig's potash apparatus attached to one of the arms, the object being to show the facility which a long beam gives to the operator, for weighing these awkward pieces of apparatus. The beam of this balance is 16 inches long. The balance, as seen in the figure, is at rest, so that a weight placed in one of the pans will not affect the equilibrium of the beam. By turning the knob in the front part of the case between the two drawers from right to left, the arm supporting the beam will descend, and the balance will be free; the oscillations of the beam will then be observed by the index moving over an ivory scale in front of the stand. The fulcrum, or centre knife-edge of the beam, works upon agate, with which, however, it is only in contact when the balance is free. The pans are suspended by fine platinum wire, and are provided with steel hooks, which hang in rings attached to the ends of the beam; these rings are ground out conically from each side, so as to form a perfect edge. The apparatus fixed on either side, above the beam, serves to move small weights along the arm, which is accurately divided into ten equal parts. This movement is effected by means of small knobs outside the case. The weight used for this purpose is made of fine gold wire, with a loop at the top. It weighs $\frac{1}{10}$th of a grain, consequently, when placed at the 1st, 2nd, 3rd, etc., division of the beam, it represents one, two, or three hundredths placed in the pan. By subdividing each division the weight may be ascertained with great accuracy, and all weights less than $\frac{1}{10}$th of a grain may be dispensed with. The knob seen above the centre of the beam can be raised or lowered, and serves to adjust the centre of gravity, which ought to be a little below the fulcrum, or centre of motion. The beam has also adjustments for bringing the ends and the centre knife-edge into the same straight line, and also for equalizing the lengths of the arms; these contrivances could not, however, be well represented in the figure.

Fig. 43 exhibits a balance of a larger description. Its beam is 18 inches long, and it is intended to carry from 2 to 3 pounds in each pan; and when loaded with such a weight it indicates distinctly $\frac{1}{50}$th of a grain. In order to obtain such a degree of delicacy with so large a weight, it is necessary that the best construction should be adopted. The beam is furnished with a straight knife-edge at each end, upon which the pans are suspended by agate planes; by this construction not only

a greater delicacy and durability, but also a greater constancy is obtained than could be arrived at with any other kind of balance. The instrument is represented in the figure as set free

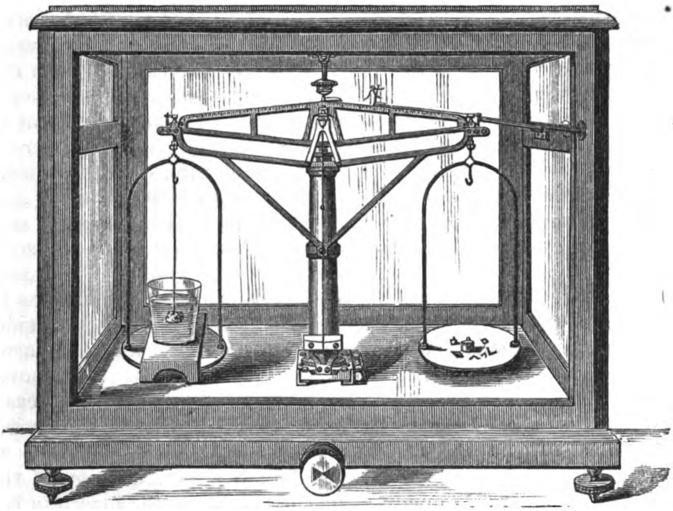


Fig. 43.

for oscillation, and on turning the knob in front from left to right, the straight arms close under the beam are raised, and receive the end pieces to which the pans are suspended by the small cylinders indicated in the figure; therefore when the balance is at rest, the centre knife-edge of the beam is taken off the agate plane of the stand, and the agate planes with the pans are taken off the knife-edges of the beam. The oscillations of this balance are also observed by an index moving over an ivory scale, in front of the stand.

The pans in this balance are made of brass, and are 6 inches in diameter; they are supported by stout brass wire, and the distance from the centre of the pans to the small brass plate to which the supporting wires are attached is $10\frac{1}{2}$ inches; evaporating dishes and flasks of considerable size may therefore be weighed, and mineral waters and filtrates contained in large beakers may be estimated by weight instead of by measure, a

method always to be preferred. Both balances are enclosed in glass cases, having convenient doors at the front and sides, and the smaller one is provided with a contrivance for steadying the pans during the operation of weighing.

In performing the process of weighing, the student will do well to observe the following rules:—1. Always to use the same pan for the same purpose, for although in a good balance it is obviously a matter of indifference which pan receives the weights, and which the substance, nevertheless, an attention to the practice of always placing the substance to be weighed in the same scale, serves in a great measure to obviate any error which may arise from inequality in the length of the arms; as, if the weights are always put into the same pan, the substance weighed in the other will be in the same proportion as the weights, though not exactly equal to them; and, in chemical experiments, proportional quantities are in general of far greater importance than *real* weights. 2. Never to place the substance to be weighed *directly* on the scale, but upon some interposed substance, as a watch glass, or, occasionally, on a piece of hot-pressed wove paper, counterpoised of course in the other scale by an equal-sized watch glass, or piece of paper, previous to putting in the weights. A substance should never be weighed while hot, in consequence of the effect produced by the ascending current of hot air, and the rushing in of a stream of cold air, which tend to give an upward motion to the pan, making it seem lighter than it really is. Substances which attract moisture from the air should be weighed in a covered crucible, or in a watch glass, the edge of which is ground so that it may be covered air-tight with another equal-sized watch glass. Another method of weighing certain substances which change in air is recommended by Faraday ('*Chemical Manipulation*,' p. 41), and may sometimes be very conveniently adopted. It consists in transferring them, not to the pan of the balance, but to a portion of water, alcohol, etc., as the case may be, of known weight, and ascertaining the increase of weight so occasioned; the analysis or experiment is then made with the solution instead of the solid body. A third important rule to be observed in weighing, is never to make any adjustment of weights or substance in the scales while the beam of the balance is free, but always to take it off its support previous to interfering in any way with the contents of the pans. The neglect of this precaution may soon entail serious injury on a delicate balance.

The following method of examining a newly purchased balance, recommended by Captain Kater, may be usefully inserted here, by way of conclusion to the few observations we have thought it advisable to make on the subject of this important instrument. 1. To ascertain whether the points of suspension and the fulcrum are in a right line, make the vibrations of the balance very slow by moving the weight which influences the centre of gravity, and bring the beam into a horizontal position by means of small bits of paper thrown into the scales. Then load the scales with nearly the greatest weight the beam is fitted to carry. If the vibrations are performed in the same time as before, no further adjustment is necessary; but if the beam vibrates quicker, or if it oversets, cause it to vibrate the same time as at first, by moving the adjusting weight, and note the distance through which the weight has passed; move the weight then in the contrary direction through double this distance, and then produce the former slow motion by means of the screw acting vertically on the point of support. Repeat this operation till the adjustment is perfect. 2. To make the arms of the beam of an equal length. Put weights in the scales as before; bring the beam as nearly as possible to a horizontal position, and note the division at which the index stands; unhook the scales, and transfer them with their weights to the other ends of the beam, when, if the index points to the same division, the arms are of equal length, but if not, bring the index to the division which had been noted, by placing small weights in one or the other scale. Take away half these weights, and bring the index again to the observed division by the adjusting screw, which acts horizontally on the point of support. If the scale-pans are known to be of the same weight, it will not be necessary to change the scales, but merely to transfer the weights from one scale-pan to the other.

146. *Weights.*—The unit of weight adopted in this country is the *grain*, and in France and Germany the *gramme.*

It must be regarded as an unfortunate circumstance, that we have in England two different sets of weights expressed by the same names. The pound and the ounce troy, and avoirdupois, have different values. The avoirdupois pound is greater than the troy pound, the former weighing 7000 grains, and the latter 5760; but as there are in the avoirdupois pound 16 ounces, while in the troy pound there are only 12, it follows, that the troy

ounce is greater than the avoirdupois ounce, the latter weighing $437\frac{1}{2}$ grains, and the former 480. In order to avoid fractions, and as there are no other grains than troy grains, troy weight is generally used for philosophical purposes.

The standard to which troy weight is referred, is the weight of one cubic inch of distilled water, which at 62° F. and 30 inches barometer weighs 252·458 grains. The troy weight table is

gr.		dwt.		oz.		lb.
24	=	1				
480	=	20	=	1		
5760	=	240	=	12	=	1

These denominations are never however employed in chemistry, the weight of substance being (when the English system is used) always reckoned in *grains*, and in the decimal divisions of the grain, viz. 0·1, 0·2, 0·3, etc., 0·01, 0·02, 0·03, etc.

The standard to which the French *gramme* is referred, is the weight of $\frac{1}{100}$th part of a cubic metre* of distilled water, at the temperature of melting ice. A gramme is equal to 15·434 grains troy, whence the following comparative table of French with troy weight.

		Gramme.		Troy grains.
Milligramme	=	·001	=	·01543
Centigramme	=	·01	=	·15434
Decigramme	=	·1	=	1·5434
Gramme	=	1	=	15·434
Decagramme	=	10	=	154·34
Hectogramme	=	100	=	1543·4
Kilogramme	=	1000	=	15434
Myriagramme	=	10,000	=	154340

The kilogramme is equal to 2 lb. 3 oz. 4·428 drachms avoirdupois, and to 2·679 lb. troy weight.

The student should assure himself once for all, on purchasing a set of weights, that they are correct among themselves, and if he has an opportunity of comparing them with standard weights, he should do so: for the purpose of adjustment, the small spherical knobs screwed into the centre of the cylindrical weights are provided with small cavities under the screws, to

* A *metre* is the ten-millionth part of the length of the meridian arc between the pole and the equator = 39·3710 English inches, though the accuracy of this measurement has been disputed.

receive portions of fine wire; a very simple method of making small weights expressing the decimal parts of a grain, is to determine with great care the weight of three or four feet of fine silver, or platinum wire, and then to cut off such portions as are equal to the weights required. The weight box, as well as the balance, must be carefully kept out of the contact of acid or other vapours; the brass weights may be gilded (previous to adjusting them) to keep them bright and clean; it is not, however, to be concluded that they necessarily become incorrect by getting tarnished, for Fresenius states, that he has examined many weights of this description, and has found them as exactly corresponding with each other in their relative proportions as when they were first used. As a general rule, however, the weights should not be touched by the hand, to prevent the necessity for which the weight boxes are provided with convenient brass forceps for the small weights, and with forks or tongs for the large ones. It is desirable to keep a shallow dish, containing quicklime, inside the glass case of the balances, in order to preserve the atmosphere in a state of dryness, and thus to prevent the oxidation of the fine steel edges and other metallic parts of the apparatus.

2. SPECIFIC GRAVITY.

147. It is very frequently an object of importance to compare the density of a substance, solid, liquid, or gaseous, with that of another substance assumed as a standard: this operation is called the determination of its *specific gravity*. The density of solids and liquids is compared with that of pure distilled water; gaseous fluids are usually compared with atmospheric air. When great accuracy is required, the temperature of the water is of importance, and in such cases it is convenient to take the temperature of the maximum density of that fluid (viz. about 39°·4 F.), at which temperature it can be more easily maintained without variations than at 62°, at which it is generally taken in this country, or at the temperature of melting ice, 32°, at which it is taken in France. Generally speaking, in the determination of specific gravities, it is sufficient to note the temperature, and to apply a correction depending on the known density of water at different degrees of the thermometer.

(I.) *Determination of the Specific Gravity of a Solid.* a. *Heavier than Water.*—This depends on the principle discovered by

Archimedes, that a body, when immersed in a fluid, loses just as much of its weight as is equal to the weight of an equal volume of that fluid; thus, supposing a piece of gold suspended from one of the pans of a balance by a fine thread or hair, to be accurately weighed in air, and then immersed in a jar of distilled water, it is evident that a quantity of water will be forced over the sides of the jar exactly equal in volume to the metal which displaces it: it is equally clear that the force with which the metal is pressed down in the water, is equal to the difference between its own weight and that of an equal bulk of water. The method proposed by Archimedes for solving the famous problem of the crown of Hero, king of Syracuse, was to immerse the solids to be compared, of known weights, in water contained in a cylindrical vessel of known area, and to note the relation between the heights at which the liquid stands, which gives the relation between their densities. The method now adopted, and which is susceptible of far greater accuracy, is to weigh the substance first in air, and then in water, and to divide the weight in air by the loss it sustains when weighed in water, the quotient is the specific gravity of the substance. Let $S =$ the specific gravity of the substance; $W =$ its weight in air; $W' =$ its weight in water; then—

$$S = \frac{W}{W - W'}$$

The method of performing the operation is shown in Fig. 43, p. 220. Thus, suppose a piece of gold to weigh in air 77 grains, and in water 73 grains, the loss in this case is 4 grains, and we have the proportion—

$$4 : 77 :: 1 : 19{\cdot}25;$$

19·25 is, therefore, the specific gravity or density of the gold.

b. *Lighter than Water.*—If the solid, the density of which is to be determined, be lighter than water, there are two ways of proceeding.

By the first method the dimensions of that part of the solid immersed, while it is floating on the surface of water, is compared with its whole magnitude; the two results bear the same proportion to each other as the specific gravity of the solid bears to that of water. The experiment is performed thus:—A glass vessel, having perpendicular sides, and as narrow as the magnitude of the solid will admit, is filled to a certain mark with distilled water; the substance is then set to float in it, and the point

to which the surface of the water rises in the vessel accurately marked: the body is then totally submerged, and the point to which the surface of the water rises again observed. The elevations of the surface produced by the partial and total submersion, indicate the portions of the solid in each case immersed, and are therefore in the ratio of the specific gravity of the solid to that of the liquid. This method is not, however, very often adopted. The following is more convenient:—The body, the density of which is to be ascertained, is attached to another which is heavier than water, and of such a size that the united weights of the two will be greater than the weight of the water which they displace, and the whole consequently sinks when immersed. The weight of the united substances is then determined, first in air, and then in water; the weight lost by immersion is equal to the weight of a quantity of water corresponding in bulk to the united bulks of the solids. The lighter solid is then detached, and the weight lost by the heavier by immersion in water ascertained; this is the weight of a quantity of water equal in bulk to the heavier solid. This loss of weight being subtracted from the loss sustained by the combined masses, the remainder is the weight of a quantity of water equal in bulk to the lighter solid; the proportion of the weight of the lighter solid to this will determine its specific gravity.

This process may be still further simplified thus:—Weigh the substance, the specific gravity of which it is desired to ascertain, first in *air*, then attach it loosely to a piece of heavy metal, the weight in *water* of which has been determined, and weigh the combined substances in water; the aggregate weight will be found less than that of the heavier body. Now subtract the weight of the lighter body from that of the heavier, and add the remainder to the weight of the former in air; we thus obtain the weight of a quantity of water equal in bulk to the lighter body, and by dividing the weight of the lighter body in air by this last-mentioned sum, the quotient is the specific gravity required.

Example.—A piece of indigo covered with a thin coating of varnish (to prevent its absorbing water) weighed in air 105·1 grains: a piece of sheet lead which was used for ballast weighed in water 124·9 grains. The indigo and the lead were now tied together, not closely, but in such a manner that the water could have free access to any part of each substance,

and weighed in water, the aggregate weight was 108·5 grains; that is, 16·4 grains lighter than the weight of the lead alone in water. Now $16{\cdot}4 + 105{\cdot}1 = 121{\cdot}5$ = the weight of a quantity of water of equal bulk to the indigo, and $\frac{105{\cdot}1}{121{\cdot}5} = 0{\cdot}865$ = the specific gravity of the indigo.

c. *Of a Powder.*—When the solid, the specific gravity of which is to be determined, is in the form of a powder, or in minute pieces, it may be placed in a cup which is counterpoised first in air, and then in water, in the usual manner; or the same method may be pursued which is adopted in taking the specific gravity of a soil. A small bottle, containing, when filled and its stopper adjusted, a certain known quantity of water, is about half filled with distilled or rain water, and a weighed quantity of the dry powder introduced. It is then well shaken, and after the solid matter has settled, it is completely filled with water, the stopper put into its place, and then weighed. The weight obtained will be obviously less than that of the united weights of the bottle full of water and the substance added, and the difference is the weight of a quantity of water equal in bulk to the solid substance added, and by dividing the weight of the powder by this difference of weight we obtain the specific gravity required.

Example.—A bottle filled with distilled water and closed with its glass stopper weighed 750 grains. About half the water was poured out, and 500 grains of a certain powder introduced. The water and the powder were well mixed by agitation, and then allowed to settle. After awhile the bottle was completely filled up with water, closed with its stopper, and weighed.

United weights of the bottle, water, and powder, (supposing the latter could have been introduced without displacing any of the water)	1250 grs.
Actual weight of the bottle, water, and powder . .	1050 „
Difference, expressing the weight of a quantity of water equal in bulk to the powder	200 „

Therefore—

$\frac{500}{200} = 2{\cdot}5$ = specific gravity of the powder.

d. *Soluble in Water.*—When the solid, the specific gravity of which has to be determined, is soluble in water, it must be

weighed in some liquid which exerts no action upon it; the density of the body is the product obtained by multiplying this number by the specific gravity of the liquid used. Thus, suppose the substance to have been weighed in oil, and its density with reference to that fluid to be 4·3, that of the oil being 0·9, then the specific gravity of the body will be $4{\cdot}3 \times 0{\cdot}9 = 3{\cdot}87$.

(II.) *Determination of the Specific Gravity of a Liquid.*—The specific gravities of liquids may be determined in two ways:—1st, by weighing them in vessels of known magnitude; and 2nd, by weighing a certain solid in the liquid to be examined, and comparing the loss of weight with that which it sustains by immersion in pure water. Bottles are sold by the philosophical instrument makers which hold, when full, and closed with their stoppers, a certain quantity, 1000, 500, or 200 grains of distilled water. The stoppers of these bottles are usually perforated, with the view of affording a free passage for the excess of fluid when the stopper is inserted in its place; there is, however, no occasion for this, and indeed it is very objectionable with corrosive fluids, such as sulphuric acid, and with volatile fluids, such as ether. For such substances M. Regnault uses a flask with a narrow neck (Fig. 44). The

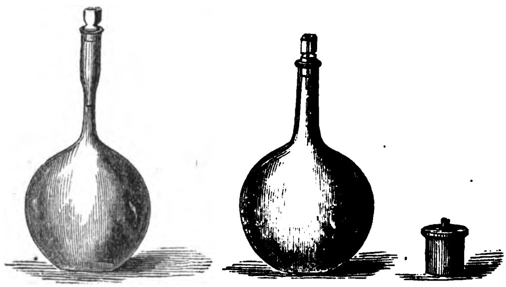


Fig. 44.

fluid is filled to the mark on the neck, and the stopper is inserted in its place; evaporation is thus rendered impossible, and should the liquid expand during the operation of weighing, no liquid can escape from the bottle in consequence of the enlargement of its neck. The bottles are accompanied with brass weights which exactly counterpoise them when empty and dry. The method of determining the specific gravity of a fluid by means of one of these bottles is very simple: we have

only to fill the bottle with the liquid in question and weigh it; its weight gives at once the specific gravity without any calculation. Thus, supposing the bottle to hold 1000 grains of distilled water at 62°, and at the same temperature, 1845 grains of oil of vitriol, and 918 grains of spirit; these numbers represent the densities of the liquids, water being 1000; or, if water be taken as unity, then the specific gravity of oil of vitriol is 1·845 and that of spirit 0·918. In determining the specific gravity of liquids in this manner, due regard must be had to temperature, otherwise the results obtained will not admit of exact comparison. The bottle should be verified before it is used, and if it should be found incorrect, that is, not to hold exactly 1000, 500, etc., grains at 62°, its capacity at that temperature must be rigorously determined once for all, and the weight of water found must be used as the divisor of the weight of any other fluid. Thus, suppose the bottle be found to hold exactly 995 grains of distilled water and 1836 grains of oil of vitriol, then $\frac{1836}{995}=1{\cdot}845=$ the specific gravity of the acid.

The determination of the specific gravity of a liquid by weighing in it a certain solid, depends on the proposition, that if a solid specifically heavier than water, and also specifically heavier than the liquid whose specific gravity is to be determined, be successively immersed in water, and in that liquid, the losses of weight will be proportional to the specific gravities of water and the liquid: and if the number expressing the loss of weight in the liquid, be divided by the number expressing the loss of weight in the water, the quotient will be the specific gravity of the liquid.

Example.—Suppose a ball of glass, when weighed in water, to lose 200 grains, and when weighed in oil of vitriol, 396 grains, then $\frac{369}{200}=1{\cdot}845=$ the specific gravity of the oil of vitriol; but suppose the same ball, when weighed in spirit, to lose 183·8 grains, then $\frac{183{\cdot}8}{200}=0{\cdot}918=$ specific gravity of the spirit.

A series of hollow bulbs of different specific gravities, called "specific gravity bulbs," are also sold by philosophical instrument makers. Their use is almost entirely confined to practical chemical operations on the large scale, though they are some-

times of great convenience in the laboratory for determining the degree of concentration of liquids. These bulbs are generally numbered. They indicate the density of the fluid by sinking or floating in it, as the case may be.

In cases where moderate accuracy only is required, the *hydrometer* is extensively exployed for the determination of the specific gravities of liquids. Its use is principally confined to commercial purposes, where expedition is of greater consequence than great exactness. The indications of these instruments depend upon the fact, that a body when it floats in a liquid displaces a quantity of the liquid equal to its own weight; and their accuracy depends upon giving them such a shape, that the part of them which meets the surface of the liquid in which they float, is a narrow stem of which even a considerable length displaces but a very small weight of the liquid. Thus any error in observing the degree of immersion, entails upon the result an effect which is inconsiderable.

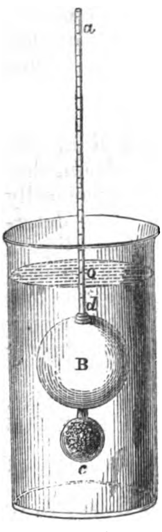


Fig 45.

The hydrometer shown in Fig. 45 is an arrangement of considerable delicacy, and is peculiarly useful for measuring the specific gravity of mineral waters; many forms have been given to the instrument.* It consists of a ball of glass, three inches in diameter, with another joining it, and opening into it, of one inch in diameter, B and *c*; and a brass neck, *d*, into which is screwed a wire *a* 0, about 10 inches long and $\frac{1}{40}$th of an inch in diameter, divided into inches and tenths of an inch. The whole weight of this instrument is 4000 grains when loaded with shot in the lower ball. It is found that when plunged into water in the jar, a grain laid upon the top *a* makes it sink one inch; therefore the tenth of a grain sinks it the tenth of an inch. Now it will stand in one kind of water a tenth of an inch lower than in another, which shows that the bulk of one kind of water equal to the bulk of the instrument, weighs one-tenth of

* For further details respecting hydrometers, and specific gravity generally, the reader may consult with advantage the Treatise on Hydrostatics, in the 'Library of Useful Knowledge,' from which the description of the hydrometer in the text is taken, and in 'Lardner's Cabinet Cyclopædia.'

a grain less than an equal bulk of the other kind of water; so that a difference in specific gravity of 1 part in 40,000 is thus detected. This weight of 4000 grains is convenient for comparing water; but the quantity of shot in the lower ball may be varied so as to make it lighter or heavier, and so adapt it to measure the specific gravities of lighter or heavier liquids. It will always be an accurate and very delicate measure for liquids of nearly the same weight. Indeed its delicacy is so great that an impurity too slight to be detected by any ordinary test, or by the taste, will be discovered by this instrument.

The most useful hydrometer for general purposes is that of Beaume. It contains for fluids heavier than water, a scale on which 0 represents the depths to which it sinks in distilled water; this is its highest point, and 15 is that to which it descends when immersed in a solution of 3 parts of *bay-salt* in 17 of water; about 50 or 60 degrees are marked between these two extreme points. In the instrument used for fluids lighter than water, 0 is marked at that point to which it sinks in a mixture of 1 part *bay-salt* and 9 water, and 10 at that where it stands in pure water. There are generally 50 degrees ascending from the lower of these points to the upper.

Fig. 46 shows the form of hydrometer (*Urinometer*) employed by Neubauer for determining the specific gravity of urine. It is graduated so as to allow the specific gravity to be ascertained within half a degree from 1·000, the specific gravity of water, up to 1·040, about the highest specific gravity of human urine, and it encloses a small thermometer fixed in the floating portion of the instrument. In reading the indications of the scale of the hydrometer, the eye should be brought to a level with the under surface of the fluid: this level is attained as soon as the hinder border of the surface of the liquid ceases to be visible; the scale is then read off at that level. If the position of the eye be not right; if it be on too high or too low a level, the surface of the fluid will take the form of an ellipse, the instrument is then pressed down a few degrees deeper into the liquid, allowed to rise freely in it, and the scale read off a second time in order to correct mistakes. In

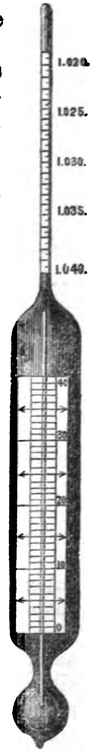


Fig. 46.

this way with a good instrument very accurate results are obtained.

(III.) *Determination of the Specific Gravity of a Gas.*—This, though simple in principle, is in practice an operation of much delicacy, and requires considerable manipulatory skill on the part of the operator. · The gas is weighed in a globe or balloon, the weight of which when empty, and when full of air, is known. The weights of the gas and of the air, are obtained by subtracting the weight of the exhausted globe from the weights of the globe filled respectively with air and gas. The quotient obtained by dividing the latter by the former, gives the specific gravity of the gas.

Regnault employs balloons of the capacity of 10 litres (1 litre = 1·76 English pint), which he counterpoises on the balance (which must be one of great delicacy) by another balloon of the same kind of glass, and of as near as possible the same bulk; the volumes of air displaced by each balloon are accurately determined by filling each with water, and weighing it first in *water* of the same temperature, and then, after carefully drying, in *air*, the difference in the two weighings giving of course the weight of the water displaced by the external volume of the balloon; the difference found in the external volumes of the two balloons is made up by attaching to the smaller a closed tube of glass, having the same external capacity in *cubic centimètres* as the weight of the water displaced is less than that displaced by the other balloon in *grammes*,—one cubic centimètre of water weighing one gramme. In this way he avoids the numerous corrections which would otherwise be required for variations in the density, temperature, and hygrometric state of the atmosphere, during the continuance of an experiment, as well as that for the displacement of air, and the adherence of a film of moisture to the glass. The balloons are suspended beneath the scale-pans of the balance in a chamber closed with glass doors to prevent currents of air. The air having been removed from the balloon as completely as possible by the air-pump, the gas the specific gravity of which is to be determined is allowed to enter; the balloon is a second time exhausted, and again filled with the gas; a third exhaustion as complete as possible is made, and the gas is allowed to enter the balloon slowly whilst it is kept surrounded with melting ice, it is then wiped with a damp cloth to prevent electrical excitation, and after the lapse of two hours weighed.

The weight having been determined with the greatest possible care, the balloon is again exhausted whilst surrounded with ice, but as a perfect exhaustion is unattainable, it is necessary to ascertain the elastic force of the gas remaining, which is done by the use of the barometric *manometer*. This instrument consists of a barometer, and a tube of similar diameter and height, but open at *both* ends, standing in the same cistern of dry mercury. The cistern is partially divided into two unequal compartments, the barometer standing in the smaller. The open end of the second tube is connected by means of a leaden pipe with the exhausted globe, mercury of course rises in the tube immediately the cock is turned, and the difference of level between the column of mercury in this tube, and that in the barometer tube, is the measure of the elastic force of the gas. The temperature during the experiment is noted.

The difference between the two weighings of the balloon represents the weight of the gas, which at 0° C. (=32° F.) fills the balloon under a pressure equal to the barometric pressure:—

Let W = The weight of the balloon and gas.
W′ = The weight of the exhausted balloon.
B = The barometric pressure.
B′ = The elastic force of the residual gas.

Then the formula—

$$(W-W')\,\frac{760}{B-B'}$$

Gives the weight of the gas at 0° C., and under the normal pressure of 760 millimètres (= 29·922 inches).

It may be useful to give here the corrections to be applied to an observed volume of gas for temperature and pressure according to the English standard. In actual analysis the more convenient French system is almost invariably adopted. The subject will be returned to, in a future chapter, where the methods of analysing nitrogenous organic substances are under consideration.

a. Corrections for temperature.—The experiments of Magnus and Regnault give as the expansion of air from 32° to 212° $\frac{366\cdot5}{1000}$ or $\frac{11}{30}$ths of its volume at 32°. The dilatation for each degree F. is according to the last observer 0·002036 or $\frac{1}{491\cdot2}$ part. It follows therefore that air at 32° expands $\frac{1}{491}$ of its bulk for every degree above, and contracts by the same amount for every degree below that temperature; 491 volumes of gas at 32° be-

come 459 volumes at 0°; it may be stated therefore that gases expand $\frac{1}{459}$th part of their volume at 0° F. for each degree; that is, 459 cubic inches at 0° become at the normal temperature, viz. 60°, 519 volumes, and at 50°, 509 volumes; hence the following simple rules for determining the volume which a gas at any observed temperature would occupy at the normal temperature.

Suppose 50 cubic inches of gas to have been observed when the thermometer was standing at 50°, then—

Volumes of air at 50°.		Volumes of air at 60°.		Observed vol. of gas at 50°.		Volume at 60°.
As 509	:	519	: :	50	:	50·98

= the volume of the gas at 60°.

Suppose the same volume of gas to have been observed when the thermometer was standing at 70°, then, as 459 volumes of air at 0° become 529 volumes at 70°, the proportions are—

Volume of air at 70°.		Volume of air at 60°.		Observed vol. of gas at 70°.		Volume at 60°.
As 529	:	519	: :	50	:	49·05

= the volume of the gas at 60°.

The reduction of the volume of a gas at any observed temperature to the volume it would occupy at 32° is attained by the use of the following formula:—

Let t = the observed temperature.
t' = the required temperature (32° F.).
x = the observed volume at t.
x' = the required volume at t'.

Then,

$$x' = \frac{(459 + t')\,x}{459 + t}$$

b. Correction for pressure.—This is very simple, for although there is reason to doubt the absolute accuracy of the law known as the "law of Marriotte," viz. that gases are expansible to an indefinite extent in proportion as the pressure upon them is diminished, and to be contractible under increased pressure exactly in proportion to the compressing force, yet the correctness at such pressures as occur naturally, and are indicated by the barometer, is generally admitted. The following is the rule for calculating the volume which a gas should possess at one pressure from its known volume at another pressure.

As the pressure to which the gas is to be reduced, is to the observed pressure or height of the barometer, so is the observed volume to the volume required. Thus, suppose the observed volume of a gas to be 120 cubic inches when the barometer is standing at 28·8 inches, we find its real volume at the normal pressure thus:—

	Normal pressure.		Observed pressure.		Observed volume.		Required volume.
As	30	:	28·8	: :	120	:	x

$$x = 115{\cdot}2 \text{ cubic inces.}$$

Suppose the same quantity of gas to have been measured when the barometer was standing at 30·6 inches, then—

$$\text{As } 30 : 30{\cdot}6 :: 120 : x$$
$$x = 122{\cdot}4 \text{ cubic inches.}$$

When the correction of a gas is to be made both for temperature and pressure, the reduction is first made for temperature, and the corrected volume is afterwards reduced according to the pressure.

(IV.) DETERMINATION OF THE SPECIFIC GRAVITY OF A VAPOUR.

a. Gay-Lussac's method.—The liquid to be experimented upon is introduced in quantities of three or four grains, into one or two little glass bulbs. The manner of filling these bulbs is as follows:—The bulb having been first accurately weighed, is warmed gently over the flame of a spirit lamp, and then allowed to cool, with its point immersed in the liquid with which it is to be filled; as the bulb cools a certain portion of the fluid enters, this is then boiled in the bulb till all the air is expelled, and the bulb is filled with the pure vapour of the substance; the point is then dipped under the surface of the liquid; as the vapour condenses, the fluid rushes up to supply its place, and the whole becomes full; the point of the bulb is then sealed by the blowpipe, and when cool it is weighed, the difference of weight gives, of course, the weight of the quantity of liquid which it contains. Two or three bulbs, being thus filled, are introduced under the edge of a narrow graduated jar, filled with, and standing over, a dish of mercury, placed upon a small furnace, or over a lamp. The jar is covered with a glass cylinder, open at both ends, and secured on the mercury dish. This cylinder is filled, above the top of the jar, with colourless oil. All things being thus arranged, the furnace or lamp is lighted;

as the temperature of the mercury and oil rises, the liquor in the little bulbs forms steam, which at length bursts the bulbs and the level of the quicksilver in the jar immediately falls, the vapour occupying the space above it. When the mercury ceases to descend, it is known that the whole of the liquid has been converted into vapour; the temperature of the oil, necessarily the same as that of the vapour, is ascertained, and by the graduation on the jar, the volume occupied by the vapour is easily read off. The weight of the vapour is known, it being that of the liquid in the bulbs; its volume at the temperature of the oil is thus found, from which its volume at the mean temperature may be calculated and compared with that of an equal weight of atmospheric air at the mean temperature and pressure.

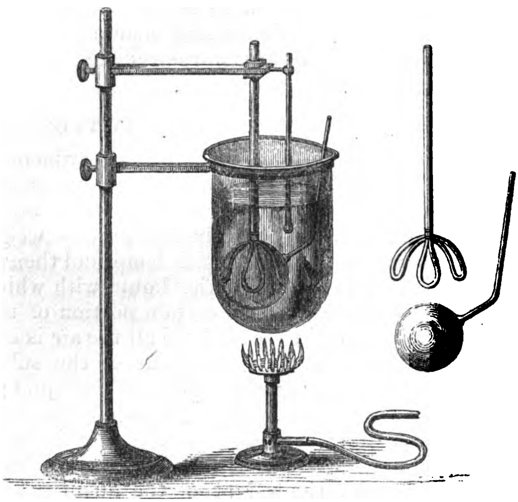


Fig. 47.

b. Dumas' method.—This is applicable to all temperatures below the melting-point of glass, and to the determination of the vapours of all substances vaporizable under that temperature, and which do not suffer decomposition by vaporization. Its discovery has therefore been of the greatest service to science,

and has led to results of the most important scientific character It is conducted as follows:—A globe of difficultly fusible glass, and capable of holding from 15 to 30 cubic inches, is first thoroughly dried; this is done by repeatedly exhausting and re-admitting air, dried by passing over long tubes filled with chloride of calcium, the globe being buried in hot sand; it is then drawn out to a long neck, having a capillary orifice; this neck is bent, as shown in the figure. It is weighed while full of atmospheric air, the temperature and barometric pressure being noted. About 120 grains of the substance to be examined are poured into a glass, (if a solid, it must be liquefied by heat,) and the globe having been warmed, its point is immersed in the liquid, and 80 or 100 grains allowed to enter; this part of the operation may be hastened by cooling the globe by dropping ether upon it. The globe is then fitted in a sort of wire cage, by which it is securely fixed in the centre of the bath in which it is to be heated, as seen in the figure. The bath is charged either with oil or with a saturated solution of chloride of calcium. The capillary beak of the tube must be long enough to project over the surface of the bath, as shown in the figure. The temperature of the bath is then increased to the desired point; when the globe becomes sufficiently heated, the liquid boils, and its vapour in passing away carries off the air which had previously filled the globe. The force of the steam increases, at first, with the temperature of the bath, by degrees it diminishes, and finally ceases altogether; the operator then knows that the excess of vapour has passed away, and that the globe is filled with the vapour of the substance, in a state of purity. Should any of the vapour have condensed in the neck of the globe, it must be chased away by a piece of red-hot charcoal. The orifice of the capillary neck is now closed air-tight by means of the blowpipe, the temperature of the bath being at the same moment carefully noted; the globe is then removed, allowed to cool, cleaned, and weighed. The next point is to ascertain exactly the capacity of the globe, with which view the extremity of the neck is broken off under mercury; this is done by first making on it a slight scratch with a file, and then plunging it underneath the surface of the fluid metal, and breaking it off by a slight tap against the side of the trough; the mercury immediately rushes into the globe, filling up the vacuum caused by the condensation of the vapour. If the experiment has been well conducted, the whole of the globe

becomes filled, but if there was a small quantity of air still remaining at the time of sealing the neck, a bubble will remain in it. The globe full of quicksilver is then emptied into a graduated jar, by which the quantity of the quicksilver being measured, the capacity of the globe is known, and all the elements for calculating the specific gravity of the vapour are thus ascertained. Thus, the volume of the globe being known, the weight of the atmospheric air it contained, is ascertained by calculation, and the globe having been weighed full of air, by deducting the weight of that volume of air, the weight of the empty globe is ascertained, and deducting this weight from that of the globe when filled with the vapour of the substance, or rather when containing the liquid resulting from the condensation of that vapour, we obtain the weight of the vapour of the substance at the temperature of the bath. The weight of the atmospheric air filling the globe at the temperature of the bath is now ascertained by calculation, by the rules already given, and this being known, the determination of the density of the vapour is made by the simple rule of proportion.

Example.—By way of illustrating this beautiful operation we quote an experiment made by the author of the process (Dumas), the weights and measures being reduced to the English standard: we have omitted certain corrections applied by the French chemists, such as that for the expansion of the glass, and the reduction of the indications of the mercurial thermometer, to those of the air thermometer, according to the experiments of Magnus; the results of these corrections not having a very significant bearing on the result.

The experiment is the determination of the specific gravity of the vapour of *camphor*.

The particulars are as follows:—

Temperature of the air	56°·3 F.
Height of the barometer	29·2 in.
Temperature of the bath at the time of sealing the balloon	471°·2 F.
Increase in the weight of the balloon	10·88 grains
Capacity of the balloon as determined by the weight of the volume of mercury required to fill it	18·0 cub. inches.

(I.) Reduction of the volume of atmospheric air which the balloon contained at the temperature, and under the atmospheric pressure, at the time of weighing it, to 32° F. and 29·9 in. barom.

α. *Correction for pressure* :—

$$\text{As } 29{\cdot}9 : 29{\cdot}2 :: 18{\cdot}0 : x$$

$$x = 17{\cdot}57$$

β. *Correction for temperature according to the formula*—

$$x' = \frac{(459 + t')\,x}{459 + t}$$

$\frac{459 + 32 \times 17{\cdot}57}{459 + 56{\cdot}3} = 16{\cdot}74$ cubic inches = the volume of air at 32° F. and 29·9 in. barom.

(II.) *Weight of this Volume of Air* :—

According to the experiments of Regnault, 100 cubic inches of atmospheric air at 32° F. and 29·9 in. barometer, weigh 32·5684 grains, therefore—

Cubic inches.		Cubic inches.		Cubic inches.		
100	:	16·74	::	32·58684	:	x

$x = 5{\cdot}455$ = the weight of the dry air with which the balloon was filled when it was weighed.

Now the increase in the weight of the balloon with its charge of camphor vapour was 10·88 grains, if therefore we add this number to the calculated weight of the air, we shall obtain the actual weight of the vapour, thus—

$10{\cdot}88 + 5{\cdot}455 = 16{\cdot}335$ = the weight of the camphor vapour.

(III.) *Reduction of the Volume of Camphor Vapour* (= 16·335 *grains*) *to* 32° *F. and* 29·9 *in. barometer* :—

α. *Correction for pressure*—

$$\text{As } 29{\cdot}9 : 29{\cdot}2 :: 18{\cdot}0 : 17{\cdot}57$$

β. *Correction for temperature*—

$\frac{459 + 32 \times 17{\cdot}57}{459 + 471{\cdot}2} = 9{\cdot}27$ cubic inches = the volume of the vapour at 29·9 in. barometer and 32° F., and which consequently weighs 16·335 grains; therefore—

100 cubic inches weigh 176·2 grains.

Now, as 100 cubic inches of air weigh at 32°, 32·58684 grains, the specific gravity of camphor vapour is found by the proportion—

$$\text{As } 32{\cdot}58684 : 176{\cdot}2 :: 1 : x$$

$x = 5{\cdot}40$ = the specific gravity of camphor vapour.

Dumas' calculation, with the corrections for the expansion of the glass globe and the reduction of the degrees of the mercurial to those of the air thermometer, gives as the density 5·52.

3. MEASURING.

148. In the quantitative examination of liquids, recourse is generally, when practicable, had to weighing, in preference to measuring. For this purpose the balanee, Fig. 43, is well adapted. When, however, it is deemed expedient to resort to the latter, the imperial pint and its subdivisions is a convenient standard for large quantities, aud the cubic inch and its subdivisions for small quantities of liquid. The measure of the imperial pint is 34·65925 cubic inches, and it contains 8750 grains of distilled water at 62° F., and at 30 in. barometer. It is divided into 20 parts, each part having a capacity of 1·7329625 cubic inches, and containing 1 ounce avoirdupois, or 437·5 grains of distilled water. The cubic inch consists of 252·456 grains of distilled water at the standard temperature and pressure, and of 3425·35 grains of mercury. Lipped jars of the imperial pint, half-pint, and quarter-pint capacity, graduated into ounces and half-ounces, are articles of commerce, aud are easily obtained. The chemist never, however, takes it for granted that these gradations are correct, but verifies each jar for himself by weighing into it successive quantities of water or mercury, and making a mark or scratch with a file or diamond at the correct division, should it not coincide with that previously made on the jar. Bottles having an exact cubic inch capacity, and holding, therefore, 252·456 grains of distilled water, and 3425·35 graius of mercury when the stopper is in its place, are also to be obtained at the philosophical instrument makers, and when correct, they are exceedingly useful, and save a great deal of time.

For the measurement of gases various sized jars are required, Figs. 48, 49, 50, 51; they are always in this country graduated into cubic inches, tenths, and hundredths; the laboratory should be furnished with a good supply of them, and some of them, as Fig. 49, should be sufficiently stout to bear, without risk, their weight when filled with mercury during the manipulations at the mercurio-pneumatic trough. As a general rule, all jars, whether for gases or for liquids, should be carefully verified before they are used for quantitative experiments; tubes in particular that are intended to be employed in gaseous analysis, must be rigorously tested; and it is better that the chemist should graduate them himself than trust to the accuracy of those met with in commerce. For this purpose, having selected

a tube of the desired size and thickness, and of clear faultless glass, it is placed in a perfectly vertical position, with its closed

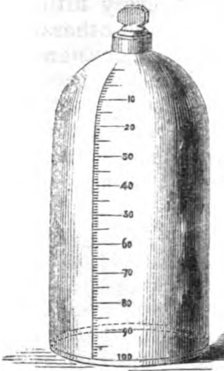


Fig. 48.

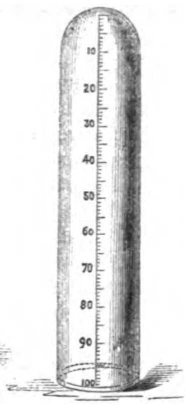


Fig. 49.

Fig. 50.

Fig. 51.

end on a flat surface. A small piece of glass tube, Fig. 52, of known capacity, the edge of which is ground so that it may be closed air-tight with the piece of ground glass, serves as a measure or gauge; this is filled with mercury, and all bubbles of air having been expelled by passing a rod of glass down the internal sides of the tube, its contents are transferred to the jar or tube to be graduated; the surface of the fluid metal is marked on the outside of the glass with a pencil. In doing this, the operator must be aware of the cohesive attraction existing between the mercury and the glass, the tendency of which is to depress that part of the surface of the metal which verges towards the sides of the tube; hence a mark made to correspond with that surface would include a space in the tube somewhat larger than that occupied by the metal. Faraday ('Chemical Manipulation,' p. 75) proposes to get rid of the difficulty by using mercury which is not quite clean, but which, from containing a little of some other metal, as tin, lead, etc., has a film formed on its surface which gives it a flat surface in the tube. A second, and a third, etc., measure of mercury is introduced and marked, till the tube is filled. It is then emptied of its contents, and covered

Fig. 52.

with a thin coat of transparent engraver's varnish, by means of a camel's-hair pencil. When dry, the pencil-marks, which are distinctly seen through the varnish, are laid bare by a sharp steel dividing-instrument, every fifth division being made somewhat longer than the others by way of distinction. The figures at each tenth division are cut through the varnish by the point of a steel pen, and the whole is then covered with hydrofluoric acid, which, attacking the glass where it is laid bare at the divisions and figures, effectually engraves them. If a relative division of the tube only is required, it is a matter of no consequence what the capacity of the little gauge may be; but when the object is to graduate tubes with reference to a standard measure,—as, for instance, the cubic inch,—then it will be found most convenient to weigh into it successive portions of mercury: thus, to divide the tube into $\frac{1}{10}$ths of a cubic inch, successive additions of 342·535 grains of mercury must be made, to divide it into $\frac{1}{100}$ths the weight of the metal must be 34·25 grains. In making the adjustments of the mercury in the pan of the balance, the small graduated pipette, Fig. 53, provided with a stop-cock and air screw, will be found very useful.

Fig. 53.

The Burette and Pipette.—For delivering small and definite quantities of liquids, as in the operations of volumetric analysis, the *burette* is an indispensable instrument. Various forms have been given to it, some of which are shown in Figs. 54, 55, 56. Fig. 54 represents Gay-Lussac's burette, which is very delicate, though rather liable to break, and not therefore so well suited as the others for the general work of the laboratory; if however pieces of cork be inserted between the two tubes, and then string bound round both, as shown in the figure, the danger of fracture will be almost entirely obviated. Being round at the bottom, it requires a support, which may be a block of wood perforated by an oval hole. Fig. 55 is known as Binks's burette; the

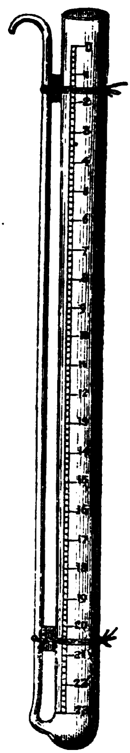


Fig. 54.

drop tube is here at the top, instead of at the bottom of the tube. The use of this instrument requires a steady hand, but after a little practice, a liquid may be delivered from it with great pre-

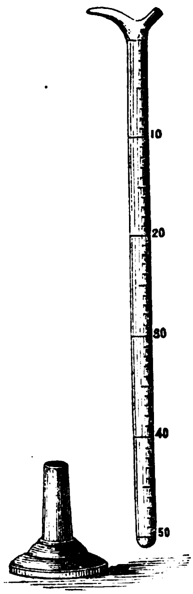


Fig. 55.

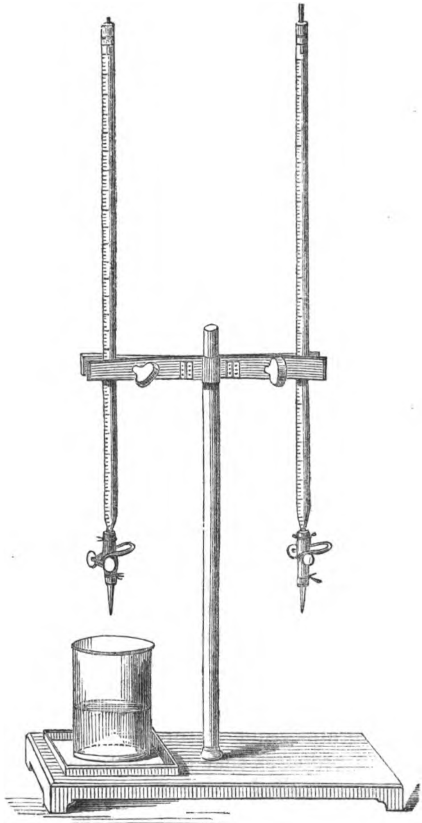


Fig. 56.

cision. Fig. 56 is Mohr's burette, which is applicable to all cases in which the contact of organic matter, such as india-rubber, is not injurious to the liquid. It consists of a graduated tube

drawn out at the end, on which is slipped a small piece of vulcanized india-rubber tubing, in the other end of which is inserted a very small glass tube as a mouthpiece. The india-rubber is confined by a brass spring, or pinchcock, (Fig. 57.)

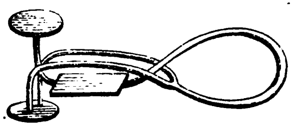


Fig. 57.

"The advantages possessed by this instrument," observes Mr. Sutton ('Handbook of Volumetric Analysis'), "are that its constant upright position enables the operator at once to read off the number of degrees of test-solution used for any analysis. The quantity of fluid to be delivered can be regulated to the greatest nicety by the pressure of the thumb and finger on the spring clip or pinchcock, and the instrument not being held in the hand, there is no chance of increasing the bulk of the fluid by the heat of the body, and thus leading to incorrect measurement, as is the case with Binks's or Gay-Lussac's form of instrument."

Burettes are graduated either in accordance with the French decimal system, or in English grains. The great advantage possessed by the former is its uniformity throughout. Thus the *cubic centimètre* is the exact measure of a *gramme* of distilled water at 4° C., or 39° F. The *kilogramme* is the weight of a cube of distilled water at the same temperature, whose side measures one décimètre; it is 1000 grammes, and occupies the volume of 1 litre, or 1000 cubic centimètres. The Binks burette should be constructed to hold 50 cubic centimètres, and of a length of about 2 feet. For the purpose of preparing standard solutions, it is convenient to have cylinders of a litre capacity, accurately graduated into 100 parts; flasks, also graduated for 100, 200, 250, 300, and 500 cubic centimètres, will also be found very convenient. When the English system is used, the burette should be constructed to hold 1000 grains, and be divided into 100 equal parts, and Mr. Sutton proposes that one of these divisions, or 10 fluid grains, should be called a *decem*, a term corresponding to the cubic centimètre, bearing the same proportion to the 10,000 grain measure as the cubic centimètre does to the litre, namely, the one-thousandth part; the same term has however been used by Mr. Ackland to represent the tenth part of a gallon. Another decimal system, constructed on the gallon measure = 70,000 grains, has been proposed by Mr. Griffin; the unit is

called the *septem*, equal to 7 grains, which bears therefore the same relation to the pound=7000 grains as the cubic centimètre does to the litre, or as Mr. Sutton's decem to the 10,000 grains. In reading burettes, the lower part of the curve formed by the surface of the liquor is taken as the true level, the observation of which is facilitated by pasting a piece of black paper on a card, so as to cover one-half of it, and then placing this card behind the burette; if this be moved until the line of separation of the two colours is about one-sixteenth of an inch below the bottom of the curve, the division may be easily read.

Of pipettes, there are two kinds,—those which deliver one certain quantity only; and those which are graduated so as to measure small quantities of solutions. The delivery pipettes (Fig. 58, *a* and *b*) have marks on their necks, indicating the amount they contain when full. It is convenient to have several of each of these pipettes of different capacities, from 100 to 10 cubic centimètres. The graduated pipette *c* is used, like the burette, for measuring small quantities of solutions. The tops of all pipettes should be circular, and narrowed slightly, so as to be more easily closed by the finger, which should be slightly moistened, in order to produce an air-tight closure. For volumetric analysis, the following graduated instruments are recommended as a useful set by Mr. Scott ('Handbook of Volumetric Analysis'):—

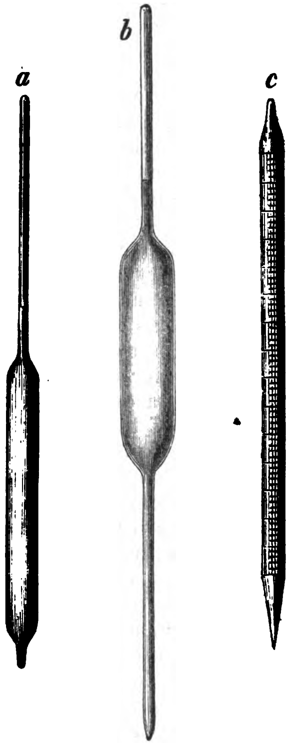


Fig. 58.

		c. c.		c. c.
One Gay-Lussac's burette,	containing	50,	graduated to	$\frac{1}{2}$
Two Mohr's burettes . .	„	100,	graduated to	$\frac{1}{2}$

		c. c.		c. c.
One Mohr's burette	. . containing	60,	graduated to	$\frac{1}{5}$
One Mohr's burette	. . ,,	20,	graduated to	$\frac{1}{10}$
One graduated pipette	. . ,,	20,	graduated to	$\frac{1}{5}$

Two graduated pipettes, containing 10 c.c., graduated to $\frac{1}{10}$ c.c.
Delivery pipettes for 1, 5, 10, 25, 100, c. c. respectively.
A mixing cylinder, to contain 1 litre, graduated to 10 c. c.
Two flasks, 1 and $\frac{1}{2}$ litre respectively.

4. DESICCATION.

149. Before the quantitative analysis of any substance can be proceeded with, it is absolutely necessary that its relations to water should be accurately ascertained. In some cases, it is merely necessary to obtain the body free from moisture previous to weighing it for analysis; in other cases, the *amount* of water present has to be ascertained. Bodies differ very much in their relative powers of absorbing and retaining water, but it is necessary carefully to distinguish between the water which a substance may contain in accidental admixture, and that which belongs to it *essentially*, being a part of its constitution; in the preliminary operation of drying, this latter water must not be interfered with. There are some salts which cannot be exposed to a dry air at common temperatures without losing the whole of their water of crystallization; others lose a part only, and others again absorb water from a moist atmosphere, eventually running into a liquid. *Sulphate* and *carbonate of soda* are examples of salts possessing the first property, viz. that of *efflorescence*, in a remarkable degree. The former, which crystallizes in six-sided prisms, contains ten equivalents, or 56 per cent. of water; by exposure to the air, it loses the whole of this water, and falls into a white powder. *Carbonate of soda*, which crystallizes in flat, oblique, rhomboidal prisms, also contains ten atoms of water of crystallization, the whole of which it loses when exposed to the air, falling, like the sulphate, into a white powder. *Common phosphate of soda* affords an example of a salt possessing the second property, viz. that of losing a part of its water of crystallization only, when exposed to the air. In its crystalline state, that of oblique rhombic prisms, it contains twenty-five equivalents, or about 62·71 per cent. of water; of these, it loses *ten* atoms by exposure to the air, and *fourteen* more at the temperature of boiling water; the remaining atom of water must exist in the

salt in a different state of combination from the others, as it is only expelled by a red-heat, and by its loss the nature of the salt is completely changed. Thus, on evaporating the aqueous solution of the salt, which has been dried at 212°, it is reproduced in its original state, viz. with twenty-five equivalents of water of crystallization; but, on evaporating a solution of the salt after it has been ignited, we obtain a salt which contains only ten equivalents of water of crystallization, and which produces, with a neutral solution of nitrate of silver, a *white* precipitate, whereas the precipitate formed by the original salt is *yellow*. As an illustration of a salt which gains water by exposure to the atmosphere, *carbonate of potassa* may be quoted. This salt may be obtained in the form of oblique rhombic octahedra, containing two equivalents of water; but, by exposure to a moist atmosphere, it speedily loses its crystalline form, and becomes liquid. *Chloride of calcium* is also a salt eminently remarkable for its power of absorbing water, a property which renders it very valuable for drying gases for experimental purposes, and for removing water from liquids, as in the rectification of alcohol.

The preparation of efflorescent and deliquescent crystals in a state fit for analysis is rather difficult; it is obviously inadmissible to expose them to the air; they must, therefore, be de-

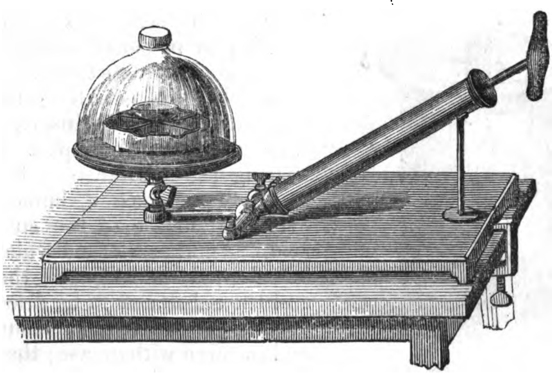


Fig. 59.

prived of their water of admixture by pressing them in a finely pulverized state between folds of bibulous paper until there are

no longer signs of moisture on the latter. There are many substances, particularly organic, which, though they do not lose their water of admixture in a dry atmosphere at common temperatures, cannot nevertheless be exposed to the temperature of 212° without undergoing decomposition. The exsiccation of these substances is effectually accomplished by placing them in convenient vessels underneath the receiver of an air-pump, in close proximity to some substance having a powerful affinity for moisture, and exhausting the air. Fig. 59 shows the arrangement; the receiver, the edge of which, ground and greased, stands on the plate of the air-pump; the substance to be dried is placed in a watch-glass or a shallow evaporating dish, supported over a shallow basin containing concentrated sulphuric acid. On exhausting the air, a liberation of aqueous vapour takes place from the substance to be dried, which is rapidly condensed upon coming into contact with the sulphuric acid, and its place supplied by fresh moisture from the substance, which is in its turn condensed as before, and thus the process goes on, the aqueous vapour travelling from the substance to the acid till it is completely dried. The desiccation of these substances may likewise be effected without the employment of the air-pump. Thus, the body may be suspended in a watch-glass from a small support over the surface of sulphuric acid contained in a beaker, as shown in Fig. 60; the edge of the beaker is ground so that it may be closed accurately by a ground glass plate *b*, in the centre of which there is a hole, through which the cork *c* is inserted, and from which the support hangs, bearing the substance to be dried in the watch-glass *d*, immediately over the surface of the sulphuric acid. Another method which may be adopted, is to place the acid and the substance to be dried on a ground-glass plate of sufficient size, and smeared with grease; the whole is covered with a well-ground receiver, and then, by raising the latter and introducing for a moment the flame of a spirit-lamp, and suddenly replacing the receiver, an imperfect exhaustion is obtained, by which the process of exsiccation is considerably facilitated.

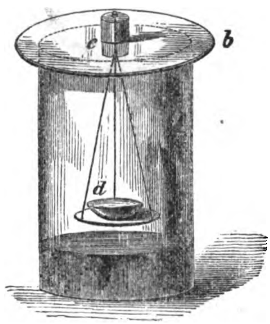


Fig. 60.

Substances which will bear the heat of boiling water may be dried in the water oven, B, Fig. 61. It consist of a copper box,

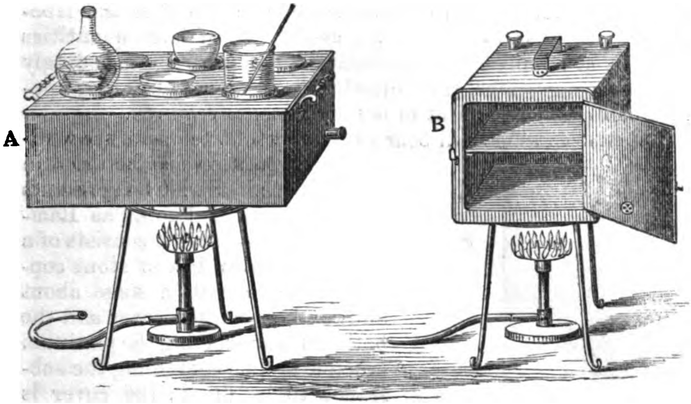


Fig. 61.

about 6 inches square, provided with a water-tight jacket or coating, the edges being soldered with brass; it is furnished with a door in which is cut a small ventilating aperture, which can be opened or closed at pleasure by means of a handle; one of the chimneys on the top of the box communicates with the jacket, through this the charge of water is given to the apparatus, it serves also for the introduction of a thermometer to enable the operator to regulate the temperature of the bath; the other chimney communicates with the interior chamber, in which the substance to be dried is placed on a watch-glass, the edge of which is ground so that it can be covered air-tight with another similar watch-glass held tightly upon it during the operation of weighing, by a clasp, as shown in Fig. 62; by this arrangement a current of air

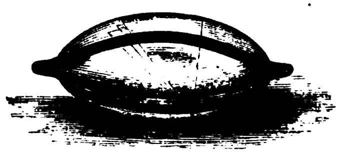


Fig. 62.

is determined through the chamber, which greatly expedites the drying of the substance. If a higher temperature than boiling water be required, the bath may be filled with a fixed

oil, such as olive oil, the temperature being regulated by the thermometer. The student must be particular not to take the weight before the glasses have got cold. The water-bath, A, Fig. 61, is an apparatus indispensable in the chemical laboratory, it serves to complete the desiccation of large quantities of liquid at an unvarying temperature, it is likewise exceedingly useful for digestions, concentrations, and numerous other operations in which the heat of boiling water is required.

Substances which will bear a tolerably high temperature without decomposition may be dried in the air-bath. Fig. 63 represents the arrangement known as Rammelsberg's air-bath; it consists of a small cylindrical box of stout copper, provided with a stage about midway between the cover and the bottom for supporting the platinum crucible or dish containing the substance to be dried; the cover is provided with two apertures, one is left open to serve as a chimney for the escape of the vapour, the other is closed with a cork, through which a thermometer passes to govern the temperature; the bath is heated over a small spirit or gas lamp on the ring of the retort stand, and by a judicious management of the flame the temperature may be kept for any length of time perfectly uniform.

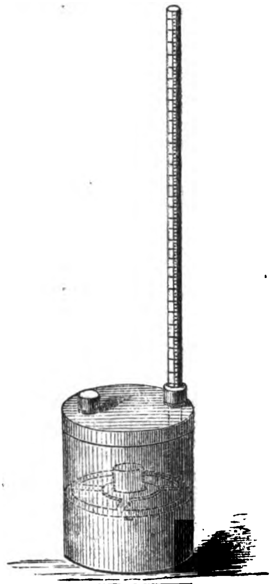


Fig. 63.

Fig. 64 represents Taylor's air-bath, and is a much more convenient apparatus than the one just described. It consists of a cylindrical box of copper or japanned tinned iron, provided with a jacket or double casing, and a false bottom pierced with holes for the more equable diffusion of air through the interior. It is provided with a thermometer for regulating the temperature, and the great advantage which it possessed over Rammelsberg's bath, besides its size, consists in its being furnished with a tall chimney, the effect of which is to determine a powerful

current of air through the chamber, thereby greatly increasing the rapidity of the desiccation. If deemed necessary, the cover of the box being closed, a tube of chloride of calcium may be adapted to the aperture seen at the bottom of the back of the box, and thus a current of dry air swept through the apparatus. The substances to be dried are placed in dishes or watch-glasses on a trellis-work of iron or copper wire, supported about an inch above the false bottom.

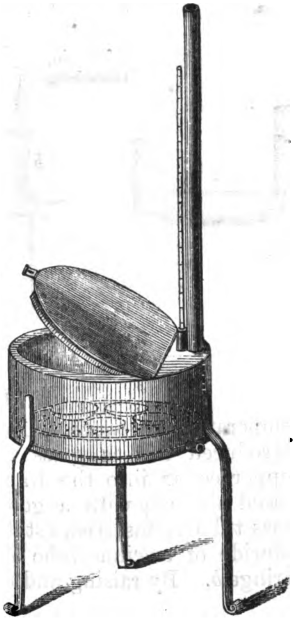
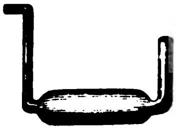


Fig. 64.

Fig. 65 represents an arrangement for drying substances in a current of dry air produced by the efflux of water. For this purpose a known weight of the substance is introduced into the small bent-glass tube which has also been weighed, the body of this tube is plunged into a copper water-bath *b*, charged with a saturated solution of common salt; it is kept in its place by a cover furnished with two apertures for the arms of the drying tube; the wider arm is united, by means of a bent tube and a caoutchouc connector containing fragments of chloride of calcium, with a tube, and the other end is connected with another chloride of calcium tube, bent at right angles so as to pass through the cork of the aspirator A, and reach down nearly to the bottom. The corks must fit the bottle perfectly air-tight, and all the joints and connections of the whole apparatus must be perfect. The bottle A is filled with water, and on exhausting the siphon it flows out in a small stream, which may be regulated by the cock *s*, its place being supplied by the air drawn through *c*, and which becomes dried during its passage through the chloride of calcium tube. The bath is charged with water, a saturated solution of common salt, or of chloride of calcium, according to the degree of heat required, and it is kept boiling by means of a spirit or gas lamp placed underneath.

Fig. 66 shows the arrangement for drying at any required



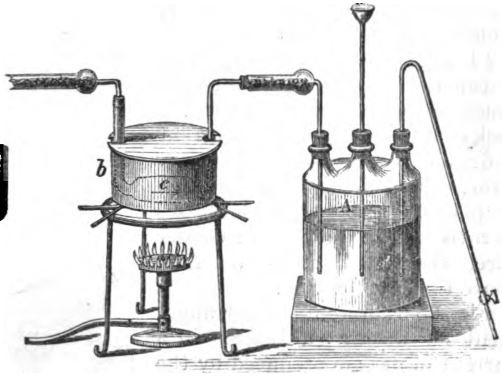


Fig. 65.

temperature *in vacuo*. The substance under examination is introduced into a glass tube *e*, which passes through a copper collar into the Rammelsberg air-bath *f*; this tube is closed air-tight with a good sound cork, into which a bent glass tube is inserted, establishing a communication with the chloride of calcium tube *d*, and finally with the exhausting syringe *b*. By raising and depressing the piston a few times, a

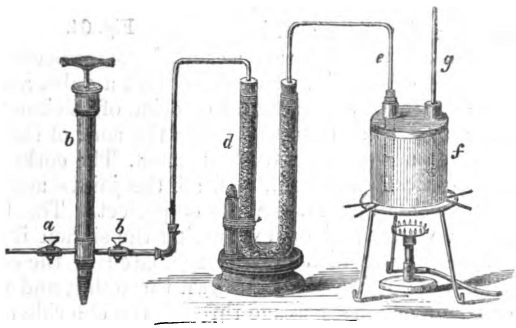


Fig. 66.

tolerable vacuum is produced in the tube, and by means of the stopcocks *a* and *c*, air may be admitted from time to time,

which becomes deprived of all moisture previous to entering the tube containing the substance, by passing over the chloride of calcium tube *d*.

In some cases it may be desirable to exclude atmospheric air altogether from contact with the substance; in such cases carbonic acid or hydrogen may be introduced into the tube *e* by connecting the stopcock *a* with a proper gasometer filled with the gas required. An apparatus contrived by Rochleder for this purpose is shown in Fig. 67. The U-shaped chloride of

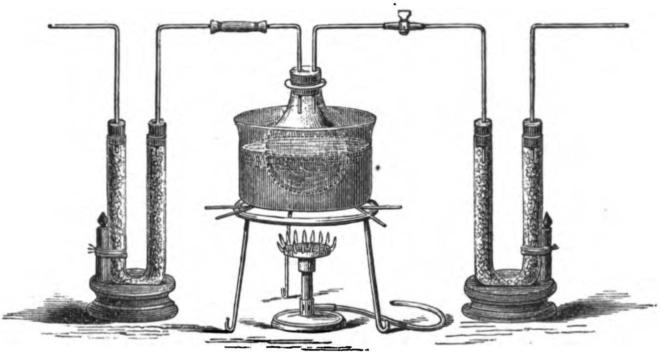


Fig. 67.

calcium tube on the right of the figure is connected by means of an india-rubber tube with a caoutchouc bag or bladder containing carbonic acid; the substance to be dried, contained in the wide glass tube, is placed in a flask immersed in an oil-bath, the temperature of which is regulated by a thermometer. The U-shaped chloride of calcium tube on the left of the figure is connected with an air-pump, and the cock being closed, the air in the flask is rarefied by a few strokes of the piston; the cock of the air-pump is then closed, and the cock communicating with the gas opened, upon which dry carbonic gas enters the flask. The operation is repeated two or three times, till the apparatus is completely filled with dry carbonic acid. The oil-bath being now raised to the requisite temperature, the flask is exhausted by the air-pump, fresh carbonic acid being from time to time admitted. The operation lasts about an hour.

In substances which will bear a red-heat without decompo-

sition, the amount of water may be determined by heating them in a combustion tube with perfectly dry *carbonate of lead*, and collecting the water expelled in a properly arranged chloride of calcium tube. The details of the operation will be understood when the methods of conducting organic analyses are described.

For the methods of conducting various other operations of quantitative analysis, such as *solution*, *precipitation*, *collecting and washing precipitates*, *evaporation*, *distillation*, etc., the student is referred to Chapter I.

CHAPTER VIII.

ON THE QUANTITATIVE ESTIMATION OF SUBSTANCES AND THEIR SEPARATION FROM EACH OTHER.

150. The following Table exhibits the *names*, *symbols*, and *chemical equivalents*, or combining proportions by weight, of the elements, according to the latest authorities. (The names of rare substances are printed in italics.)

Symbol.	Element.	Equivalent Number. H=1.	Principal Compounds with Oxygen.
Al	Aluminum	13·75	Al_2O_3, Alumina.
Sb	Antimony (Stibium) .	122·0	SbO_3, SbO_4, SbO_5
As	Arsenic	75·0	AsO_3, AsO_5: arsenious acid, arsenic acid
Ba	Barium	68·5	BaO, BaO_2
Bi	Bismuth	210·0	BiO_3
B	Boron	10.9	BO_3: boracic acid
Br	Bromine	80·0	BrO_5
Cd	*Cadmium*	56·0	CdO
Ca	Calcium	20·0	CaO
C	Carbon	6·0	CO, CO_2
Ce	*Cerium*	46·0	Ce_2O_3
Cl	Chlorine.	35·5	ClO, ClO_3, ClO_5, ClO_7
Cr	Chromium	26·27	Cr_2O_3
Co	Cobalt	29·5	CoO
Cs	*Cæsium*	133·0	CsO
Cu	Copper (Cuprum) . .	31·75	Cu_2O, CuO
D	*Didymium*	48·0	DO
E	*Erbium*		
F	Fluorine	19·0	
G	*Glucinum*	4·66	GO
Au	Gold (Aurum) . . .	196·66	AuO_3
H	Hydrogen	1·0	HO, HO_2
Il	*Ilmenium*		
I	Iodine	127·0	IO_5, IO_7

Symbol.	Element.	Equivalent Number. H=1.	Principal Compounds with Oxygen.
Ir	*Iridium*	98·56	Ir_2O_3
Fe	Iron (Ferrum). . . .	28·0	FeO, Fe_2O_3, FeO_3
La	*Lantanium*	46·0	LaO
Pb	Lead (Plumbum). . .	103·5	PbO, PbO_2
Li	*Lithium*	7·0	LiO
Mg	Magnesium.	12·16	MgO
Mn	Manganese	27·5	MnO, Mn_2O_3, MnO_2, MnO_5, MnO_7
Hg	Mercury (Hydrargyrum)	100·0	Hg_2O, HgO.
M	*Molybdenum*	48·0	MO, MO_2, MO_3
Ni	Nickel	29·5	NiO
Nb	*Niobium*	48·8	NbO_2
N	Nitrogen	14·0	NO, NO_2, NO_3, NO_4, NO_5
Os	*Osmium*	99·5	OsO, Os_2O_3, OsO_2, OsO_3, OsO_5
O	Oxygen	8·0	HO
Pd	*Palladium*	53·24	Pd_2O, PdO, PdO_2
P	Phosphorus	31·0	P_2O, PO, PO_3, PO_5
Pt	Platinum	98·56	PtO, PtO_2
K	Potassium (Kalium) . .	39·0	KO, KO_3
Ro	*Rhodium*	52·16	RoO, Ro_2O_3
Ru	*Ruthenium*	52·11	RuO, Ru_2O_3, RuO_2, RuO_3
Rb	*Rubidium*	85·36	
Se	*Selenium*	39·75	SeO_2, SeO_3
Si	Silicon	14·0	SiO_2
Ag	Silver (Argentum) . .	108·0	Ag_2O, AgO, AgO_2
Na	Sodium (Natrium) . .	23·0	NaO
Sr	Strontium	43·75	SrO
Ta	*Tantalum* or *Columbium*	68·80	TaO_2
Te	*Tellurium*	64·50	TeO_2, TeO_3
Tb	*Terbium*	?	TbO
Tl	*Thallium*	202·96	TlO
Th	*Thorinum*	59·5	ThO
Sn	Tin (Stannum) . . .	59·0	SnO, SnO_2
Ti	*Titanium*	25·0	TiO, TiO_2
W	Tungsten (Wolfram). .	92·0	WO_2, WO_3
U	Uranium	60·0	UO, U_2O_3
V	*Vanadium*	68·5	VO, VO_2, VO_3
Y	*Yttrium*	32·0	YO
Zn	Zinc	32·75	ZnO
Zr	Zirconium	44·75	ZrO_2

In describing the methods to be pursued for bringing the several substances mentioned in the above Table into a state fit for estimation, and for separating them quantitatively from other substances, we shall follow, as nearly as possible, the same arrangements which we adopted in treating of the com-

portment of substances with reagents, viz. arrange them into a series of groups. With respect to the bases there will be no difficulty in following out this method: in treating of the acids, a variation may probably appear desirable.

I. BASES.

GROUP I.

The Metals of the Alkalies proper: Potassium, Sodium, Ammonium, Lithium.

151. Potassium.

This metal is quantitatively estimated as *sulphate*, as *chloride*, as *nitrate*, and as *double chloride of platinum* and *potassium*.

Quantitative determination as Sulphate.—Potassium is in general estimated in the form of this salt when no other bases are present; the solution containing it must be carefully evaporated to dryness, and the residue dried for some time before it is transferred to a platinum crucible to be ignited; this precaution is necessary, to guard against a loss from decrepitation. It fuses at a strong red-heat, and at a very high temperature it volatilizes. Its composition is—

One equivalent of KO . . .	47 . .	54·02
One equivalent of SO_3 . . .	40 . .	45·98
One equivalent of KO,SO_3 .	87 . .	100·00

If the solution contain excess of sulphuric acid, the *hydrated bisulphate* is obtained by evaporation; this salt must be reduced to the neutral sulphate, which is done by igniting it in a platinum crucible containing a fragment of carbonate of ammonia, and loosely shut with its cover, the excess of sulphuric acid flies off in an atmosphere of carbonate of ammonia; a gentle ignition must be continued till the salt assumes the solid state, the neutral sulphate being far less fusible than the acid sulphate.

Quantitative estimation as Nitrate.—When the alkali exists in a solution in the form of nitrate it may be weighed as such; it should not be fused, as it is thereby partially decomposed. It is anhydrous. Its composition is—

One equivalent of KO . . .	47 . .	46·54
One equivalent of NO_5 . . .	54 . .	53·46
One equivalent of KO,NO_5 .	101 . .	100·00

Quantitative estimation as Chloride.—Potassium may likewise be weighed in the form of this salt, when it exists as such, in a solution. It should not be heated above feeble redness, and the crucible should be loosely covered, or a loss may be sustained. Its composition is—

One equivalent of K . . .	39	. . 52·35
One equivalent of Cl . . .	35·5	. . 47·65
One equivalent of KCl . .	74·5	100·00

Quantitative estimation as double Chloride of Platinum and Potassium.—For this purpose the alkali must be in the state of chloride, the solution is evaporated to a small bulk, and excess of bichloride of platinum and free hydrochloric acid added; the mixture is then evaporated to dryness on the water bath, and the crystalline residue digested with spirits of wine, which removes the excess of bichloride; it is then transferred to a weighed filter, washed with spirits of wine and dried at 212°. It composition is—

One equivalent of K .	39	. 16·00	= 19·262 KO
One equivalent of Pt .	98·50	. 40·37	
Three equivalents of Cl.	106·5	. 43·63	
One equiv. $KCl,PtCl_2$.	244·00	100·00	

If the operator be certain that no other base but potassa is present, and that it exists in the solution in the state of neutral sulphate, or as chloride of potassium, it may then be determined in an *indirect* manner, by estimating the sulphuric acid as sulphate of baryta, or the chlorine as chloride of silver, and calculating the amount of alkali present from the quantity of sulphuric acid, or of chlorine, thus obtained.

152. Sodium.

This metal is quantitatively determined as *sulphate*, as *carbonate*, and as *chloride*.

Quantitative estimation as Sulphate.—The same method is followed as with sulphate of potassa. It does not decrepitate. Its composition is—

One equivalent of NaO . .	31·0	. . 43·66
One equivalent of SO_3 . .	40·0	. . 56·34
One eqvivalent of NaO,SO_3	71·0	. . 100·00

Quantitative estimation as Chloride.—The salt must be well

dried before it is ignited, to prevent decrepitation; the crucible should be loosely covered. Its composition is—

One equivalent of Na	. 23·0	. 39·31	= 52·99 NaO
One equivalent of Cl	. 35·5	. 60·69	
One equivalent of NaCl	58·5	100·00	

Quantitative estimation as Carbonate.—As carbonate of soda does not attract moisture from the air so rapidly as the corresponding potassa salt, sodium may be weighed as such. It may be fused without volatilization or decomposition. Its composition is

One equivalent of NaO . .	31·0 . .	58·49
One equivalent of CO_2 . .	22·0 . .	41·51
	53·0	100·00

153. *Separation of Soda from Potassa.*—The mixed alkalies are converted into chlorides; in most cases this may be done by simply digesting and evaporating with hydrochloric acid; if, however, the alkalies are combined with sulphuric acid, that acid must first be precipitated by chloride of barium, and the excess of baryta removed by carbonate of ammonia mixed with a little caustic ammonia; the solution is filtered, and the filtrate is evaporated to dryness, and ignited, the residue is redissolved in hydrochloric acid, and the alkalies are thus brought to the state of chlorides.

If the alkalies are combined with *phosphoric acid*, the solution is evaporated to dryness, ignited, redissolved in water, and precipitated by neutral *nitrate of silver;* the fluid is filtered from the precipitated phosphate of silver, and the excess of nitrate of silver is removed by hydrochloric acid.

If the alkalies are in combination with *boracic acid*, the best method of separating them is by decomposing the boracic acid into gaseous fluoride of boron; for this purpose the dry compound is digested in a platinum crucible with 3 or 4 parts of pure powdered fluor-spar and concentrated sulphuric acid, and the heat is continued as long as fumes continue to be evolved, the alkalies are thus converted into sulphates, which are changed into chlorides as above directed.

The mixed alkaline chlorides, being carefully weighed, are dissolved in a small quantity of water and mixed with excess of an aqueous solution of bichloride of platinum, the solution is evaporated to dryness on the water-bath, and the dry mass

is treated with a mixture of ether and spirits of wine; the potassium is estimated as above described; the spirits of wine poured on the evaporated residue must acquire a yellow colour, if it does not, it is a proof that sufficient bichloride of platinum has not been added, and the experiment must be repeated with a fresh portion. Berzelius recommends to mix the dry chlorides with $3\frac{3}{4}$ times their weight of the crystallized double chloride of platinum and sodium, a quantity just sufficient to convert the whole mass into double chloride of platinum and potassium, supposing it to consist *entirely* of chloride of potassium; the process is conducted precisely as before. The soda is either calculated from the difference between the quantity of chloride of potassium found, and the original weight of the mixture analysed, or in a *direct* manner, as follows:—the filtrate from the double potassium salt is mixed with solution of *sal ammoniac* in excess, and strong alcohol added; all the platinum salt is thus removed, and the colourless filtrate being evaporated to dryness, the residue is gently ignited and weighed as *chloride of sodium*.

Maumené's method.—For industrial operations, an approximate result may, according to *Maumené*, be attained by adding to the mixture of the new alkalies a salt of alumina, and calculating the amount of potash from the weight of the *alum* formed.

Pagenstecher's method of estimating the amount of Soda in crude Potash. (Chem. Gaz., January, 1848.) This is founded on the property possessed by a saturated solution of sulphate of potassa of still dissolving a large amount of sulphate of soda. A certain weight of the sample to be examined is mixed with water, and sulphuric acid added to it until the liquid has an acid reaction; it is then evaporated to dryness, and the residue ignited and weighed. The powdered saline mass is well agitated in a graduated cylinder with six times its weight of a concentrated solution of sulphate of potassa, the liquid drawn off the sediment with a siphon, and the same quantity of the solution of the sulphate of potassa again poured over the residue. After some time the residue is brought upon a weighed filter, the funnel covered during filtration, the filter, when the liquid has drained off, weighed moist, and again, after being dried at 212°, the difference is the evaporated water of the solution of sulphate of potassa, the degree of concentration of which is known. It is known, therefore, how much of the

salt was dissolved in the evaporated water; this quantity is subtracted from the weight of the saline residue. If the potassa were free from soda, the weight of the sulphate of potassa now remaining must be the same as that first obtained; but if it contained soda, this has been removed as sulphate of soda, and the weight of the first saline residue has been reduced. From the loss, the amount of the soda present can be calculated; if the loss = V, the amount of the soda is calculated thus:—

Eq. of NaO,SO_3.		Eq. of NaO,CO_2.				
71	:	53	::	V	:	x

x = amount of carbonate of soda present in the specimen.

It should, however, be observed that when soda is used to adulterate potassa, a kind is employed that contains about 20 per cent. of sulphate of soda. Before making the weighings, it is well to take the specific gravity of the filtered solution of the sulphate of potassa; if it be the same as before it can have removed nothing, and if it has taken up sulphate of soda its density has naturally been raised.

Indirect separation of Potassa from Soda.—This method is founded on the difference which exists between the combining numbers of potassium and sodium, and is applicable to both sulphates and chlorides. It is deduced from the following considerations:—Suppose the alkalies to be in a state of sulphates, and 100 grains of the mixture to have yielded 153 grains of sulphate of baryta=52·6 grains of sulphuric acid. Let the quantity of *sulphate of potassa* present be called A, and that of *sulphate of soda* B: then A+B=100, or 100—B=A. That is, the proportion of sulphate of potassa in the mixture, is the weight of the mixture analysed *minus* the proportion of sulphate of soda.

Now one part of sulphate of
potassa contains . . . . ·4598 sulphuric acid.
And one part of sulphate of
soda contains . . . . ·5634 ditto.

The 52·6 grains of sulphuric acid found in the mixture must therefore be $(A \times \cdot4598) + B \times \cdot5634$; that is, the number of units present of *sulphate of potassa* multiplied by the quantity of sulphuric acid in *one* unit, added to the number of units present of *sulphate of soda* multiplied by the quantity of sulphuric acid in *one* unit:—

$$(A \times \cdot 4598) + (B \times \cdot 5634) = 52 \cdot 6$$

$$\text{consequently } A = \frac{52 \cdot 6 - (B \times \cdot 5634)}{\cdot 4598};$$

but A has been shown above to be $= 100 - B$; substituting this value, therefore, for A, we have—

$$100 - B = \frac{52 \cdot 6 - B \times \cdot 5634}{\cdot 4598}$$

$$\text{or, } 100 \times \cdot 4598 - (B \times \cdot 4598) = 52 \cdot 6 - (B \times \cdot 5634)$$

$$\text{or, } 45 \cdot 98 - (B \times \cdot 4598) = 52 \cdot 6 - (B \times \cdot 5634)$$

and, putting the two B's on the same side of the equation, we have $(B \times \cdot 5634) - (B \times \cdot 4598) = 52 \cdot 6 - 45 \cdot 98$

$$\text{or, } B = \frac{52 \cdot 6 - 45 \cdot 98}{\cdot 5634 - \cdot 4598} = \frac{6 \cdot 62}{\cdot 1036} = 63 \cdot 9$$

The mixture contains, therefore, 63·9 per cent. of sulphate of soda, and 36·1 per cent. of sulphate of potassa.

Suppose the alkalies to be in the state of chlorides, and 133 grains of the mixture to have given 287 grains of chloride of of silver $= 71$ grains of chlorine;

Then let the quantity of chloride of potassium be . . A
And that of chloride of sodium . . . . B

$$\text{then } A + B = 133; \text{ and } A = 133 - B.$$

Now one part of chloride of potassium contains . . . . ·4765 chlorine
And one part of chloride of sodium contains ·6069 ditto.

Therefore, as before, $71 = (A \times \cdot 4765) + (B \times \cdot 6069)$,

$$\text{consequently } A = \frac{71 - (B \times \cdot 6069)}{\cdot 4765}$$

$$\text{or, } 133 - B = \frac{71 - (B \times \cdot 6069)}{\cdot 4765};$$

$$\text{or, } 133 \times \cdot 4765 - (B \times \cdot 4765) = 71 - (B \times \cdot 6069);$$

$$\text{or, } 63 \cdot 38 - (B \times \cdot 4765) = 71 - (B \times \cdot 6069);$$

$$\text{and } (B \times \cdot 6069) - (B \times \cdot 4765) = 71 - 63 \cdot 38;$$

$$\text{therefore } B = \frac{71 - 63 \cdot 38}{\cdot 6069 - \cdot 4765} = \frac{7 \cdot 62}{\cdot 1304} = 58 \cdot 43.$$

The mixture is therefore composed of 58·43 grains of chloride of sodium, and 74·57 grains of chloride of potassium.

From the above calculations the following rule for the indirect determination of soda and potassa, when together present in a mixture, in a state of sulphates, is derived :—

From the *quantity of sulphuric acid subtract the product obtained by multiplying the weight of the mixture into the quantity of sulphuric acid in a unit of sulphate of potassa, and divide the remainder by the difference between the quantity of sulphuric acid in a unit of sulphate of soda, and the quantity in a unit of sulphate of potassa; the quotient is the quantity of sulphate of soda in the mixture.*

Example.—In 100 grains of a mixture of the two sulphates, 50 grains of sulphuric acid are found.

$$\frac{50-(100 \times \cdot4598)}{\cdot5634-\cdot4598} = \frac{50-45\cdot98}{\cdot1036} = \frac{4\cdot02}{\cdot1036} = 38\cdot8 =$$

the sulphate of soda; consequently,

$100-38\cdot8=61\cdot2=$ the sulphate of potassa.

The same rule applies to the determination of the alkaline chlorides, substituting chlorine for sulphuric acid; the results are tolerably accurate, but the determinations of sulphuric acid and chlorine must be made with the greatest care.

154. *Alkalimetry.*—The commercial value of the several varieties of potassa and soda depends on the amount of carbonated or caustic alkali which they contain; it is important therefore to the purchaser of these articles, to be in possession of a simple and expeditious method of determining with tolerable accuracy the amount of available alkali in the crude salt; a complete chemical analysis of such a heterogeneous mixture requiring great skill and time. Two methods are adopted for this purpose: the *first*, that of Gay-Lussac, depends on the constant saturating power of sulphuric acid of a certain determinate strength, being founded in common with every other process involving chemical combination or decomposition, on the law of definite proportions; the *second*, that of Fresenius and Will, depends on the determination of the amount of carbonic acid evolved from a given weight of the salt during its decomposition by sulphuric acid.

(I.) *The Volumetric process* (modification of Gay-Lussac's method).

(a.) *Preparation of the standard acid.*—Ordinary oil of vitriol is diluted with ten or twelve parts by measure of water, and the mixture allowed to cool. A quantity of the best bicarbonate of

soda is washed on a filter with cold distilled water, till the filtrate when neutralized with pure nitric acid ceases to give a precipitate either with nitrate of silver or chloride of barium; it is then well dried, and heated to low redness for some time in a porcelain or platinum crucible; when cold it is weighed, again heated for some time, and then again weighed; the process is complete, that is, the second atom of carbonic acid has been completely expelled, when the weight remains constant. Of the purified carbonate of soda thus prepared, 530 grains are dissolved in exactly 10,000 grains of distilled water, a solution is thus obtained, 1000 grain measures of which contain 53 grains, representing one equivalent of carbonate of soda. This quantity of the alkaline solution is poured into a small beaker, and a sufficient quantity of infusion of litmus is added to communicate to it a distinct blue colour. The burette is filled exactly to 0 with the diluted acid, and the beaker being placed on a small sand-bath over a lamp, the acid is poured in until the blue colour is changed to a bright red; the operator must be careful not to mistake the *wine-red* colour which the liquor assumes from the evolution of carbonic acid, for the distinct red produced by a very slight excess of the acid, and when the point of saturation is approached, the addition of the acid must be made with great care, the alkaline liquid being in a state of ebullition. The operation being finished, the quantity of acid which has been required, is observed, and the experiment is repeated again and again, on fresh 1000 grain measures of the alkaline solutions, until perfectly concordant results are obtained.

Suppose that 600 grain measures of acid have been required to effect an exact saturation of the alkaline solution, this then is the quantity of acid equivalent to 53 grains of carbonate of soda, and by adding 400 grain measures of water to every 600 grain measures of such acid, a solution is obtained, 1000 grain measures of which contain exactly 49 grains of HO,SO_3 equivalent therefore to 53 grains of carbonate of soda, to 40 grains of hydrate of soda, to 69 grains of carbonate of potassa, and to 56 grains of hydrate of potassa.

Mohr prefers oxalic to sulphuric acid, for the following reasons:—1st, because it is easily obtained in a state of purity by recrystallization, and in its crystalline form its composition is perfectly definite ($C_2O_3HO, + 2HO$); 2nd, because being a solid it is better adapted for weighing than a liquid, and is not

liable to deliquesce or effloresce; and 3rd, because it is quite fixed in heated solutions.

If oxalic acid be adopted as the base of the volumetric alkalimetrical system, 63 grains of the pure crystallized acid are dissolved in water, and the solution diluted to 1000 grain measures at 60° F. This quantity of solution will then neutralize exactly 40 grains of hydrate of soda, or 56 grains of hydrate of potassa, and 53 grains of carbonate of soda, and 69 grains of carbonate of potassa. In order accurately to control this solution, Mohr tests it with a solution of caustic potassa or soda; he prefers the former, as it has less action on the glass. Scott prefers caustic soda, from the greater facility with which it may be obtained free from silicic and sulphuric acids. It is immaterial which alkali is employed. The caustic solution is diluted with distilled water until it is exactly equal in strength to the normal acid. It is preserved in a bottle, through the stopper of which is inserted a tube containing a mixture of equal parts of Glauber's salt and quicklime, previously mixed together, dried, and ignited.

(b.) *Performance of the Alkalimetrical assay.*—When a sample of commercial soda has to be tested, 530 grains, or a submultiple of that quantity, should be weighed out from the thoroughly powdered and mixed sample; after being dried, it should be gently ignited in a porcelain or platinum crucible, and allowed to cool without exposure to the air, or under the receiver of the air pump, as represented in Fig. 59; when cold, it is again weighed; the loss indicates the amount of moisture. It is then washed into a beaker, in which it is dissolved; should any insoluble residue remain, it is filtered off, dried, and weighed; the clear filtrate is made up to exactly 10,000 grain measures, supposing 530 grains to have been taken, or to 5000 grain measures, supposing half that weight to have been used. The solution is well mixed together, and from it 1000 grain measures are taken, transferred to a beaker, the solution rendered blue with litmus, heated to boiling, and then tested with the normal acid in the manner just described, until the neutral point is reached; the process may be repeated several times, if necessary, to be certain of the accuracy of the analysis. In order however to avoid all ambiguity arising from the carbonic acid, a sufficient quantity of acid may be added to render the liquid very decidedly red, and then the normal caustic alkali added drop by drop, until the liquid suddenly changes to violet-blue;

the number of divisions of the burette that have been required to effect this, must be deducted from the quantity of acid originally used; by this "backward" or "residual" method very sharp results are obtained.

Suppose 850 burette divisions of the normal acid have been required, the following calculation gives the amount of real carbonated alkali in the sample :—

As 1000 : 850 :: 53 : x

$x = 45$, the amount of carbonate of soda in 53 grains of the sample.

The carbonate of soda of commerce sometimes contains two or three salts arising from imperfect decomposition, which interfere with the accuracy of the alkalimetrical assay. These salts are *sulphide of sodium* (NaS); *hyposulphite of soda* (NaO,S_2O_2); *and sulphite of soda* (NaO,SO_2); the presence of the former is indicated by the solution blackening salts of lead; all error arising from the presence of these salts is removed by evaporating the solution to dryness after the addition of a few crystals of chlorate of potassa, and heating the residue; the sulphur is hereby converted into sulphuric acid, which is harmless.

It is true that if *hyposulphites* are present another error is introduced, S_2O_2 becoming by oxidation $2SO_3$, so that one equivalent of sulphuric acid is free to neutralize one equivalent of alkali, but as it is very seldom that this oxygen compound of sulphur is present in quantity, it is of little practical importance.

But the sample may contain *caustic* soda, as is the case with the crude soda of commerce, and the alkaline leys used in soda, paper, and other manufactures.

Now as the above alkalimetrical process makes no distinction between carbonated and caustic alkalies, both exerting the same action on litmus, and both being converted into sulphates by sulphuric acid, it is necessary in the examination of such mixtures to determine the amount of carbonic acid by an independent experiment. This object is accomplished by adding to a hot solution of the salt, chloride of barium as long as a precipitate takes place, this precipitate contains in the form of carbonate of baryta all the carbonic acid which existed in the sample in the form of carbonated alkali; it is collected on a filter, washed rapidly without exposure to the air, and the amount of carbonic acid determined by one of the processes recommended

under "Carbonic acid." The amount of carbonic acid being thus determined, also by the volumetric assay of another portion of the sample, the total amount of alkali; the relative proportions of carbonated and caustic alkali are easily ascertained.

In the examination of commercial pearlashes, the mode of operating is precisely the same, but as the equivalent of carbonate of potassa is 69, the weight of the sample to be operated upon to make in solution 10,000 grain measures, will be 690 grains. It may sometimes be convenient to employ a normal sulphuric acid, 1000 grain measures of which shall be equivalent to precisely 100 grains of the anhydrous caustic alkali; for this purpose it is obvious that different standard acids will be required for soda and for potassa, that for soda must be of such a strength that 1000 grain measures shall saturate exactly 171 grains of pure carbonate of soda, and that for potassa must be precisely equivalent to 146·8 grains of pure carbonate of potassa, the advantage of the standard acid above described is its equivalency both to potassa and soda.

Mr. Scott ('Handbook of Volumetric Analysis') gives the following directions for preparing the infusion of litmus:—"Treat 1 lb. of litmus with about 7 or 8 lbs. of water, raise the whole to the boiling-point, and then after having allowed to cool slightly, throw on a filter in order to remove the mineral and other impurities always present in the commercial article. The solution thus prepared should be kept in an *open* bottle, as if the air be

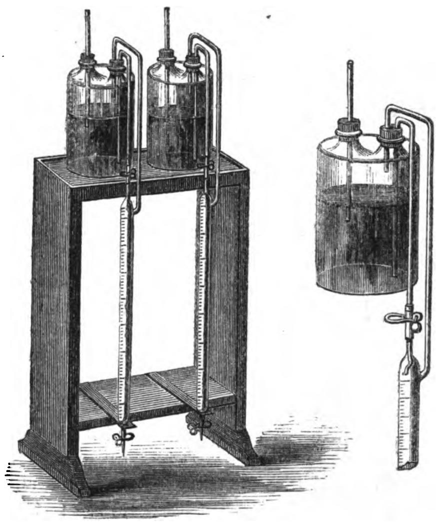


Fig. 68.

not allowed access to it, it is very liable to undergo decomposition, the addition of a little spirit improves its stability. A fixed quantity for use in each analysis should be taken out by means of a small graduated pipette, in order to ensure the same intensity of colour in each analysis. The infusion of litmus is slightly alkaline, but it may be rendered perfectly neutral, by boiling with a small quantity of chloride of ammonium.

Those who are engaged in the frequent practice of alkalimetrical assays, will find it very convenient to prepare large quantities of normal solutions of acid, and caustic alkali, and to keep them in large Wolfe's bottles, mounted on a convenient stand, as in Fig. 68. The acid should be coloured red by the addition of a few drops of infusion of litmus, and the alkali blue. The manner of arranging the pipettes so that they may be filled without detaching them from the apparatus, will be understood from a simple inspection of the figure. The air-tube of the bottle containing the normal caustic alkali, may be replaced by a wider tube containing a mixture of Glauber's salt and quicklime previously ignited.

(II.) *Method of Fresenius and Will.*—The alkalimetrical process above described seeks its object by determining the amount of *alkali*, calculating it from the measure of acid which it requires for its neutralization. In the method now to be described the result is obtained by determining the quantity of *carbonic acid* with which the alkali was combined.

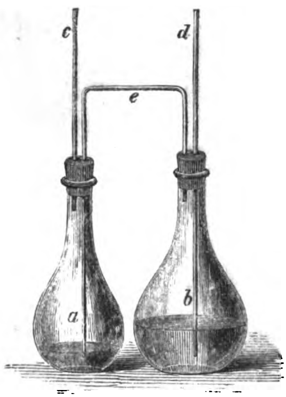


Fig. 69.

The process is conducted as follows (Fig. 69):—

a and *b* are two flasks. Wide-mouthed medicine bottles even may be employed. *b* should have a capacity of from 2½ to 2 ounces of water: it is advisable that *a* should be somewhat smaller, say of a capacity of about 1½ to 2 ounces. Both flasks are closed by means of doubly perforated corks: these perforations serve for the reception of the tubes, *c*, *d*, and *e*. All these tubes are

open at both ends; when operating, the end of the tube *d* is closed by means of a small piece of wax. The substance to be examined is weighed and projected into the flask *b*, into which water is then poured to the extent of one-third of its capacity; *a* is filled with common English sulphuric acid to about half its capacity. Both flasks are then corked, and the apparatus is weighed. The air in the whole apparatus is then rarefied by applying suction to the tube *c*; the consequence is, that the sulphuric acid contained in *a* ascends into the tube *e*, and thus a portion of it flows over into *b*; immediately upon its coming into contact with the carbonate contained in this flask, the evolution of carbonic acid begins briskly. The peculiar construction of the apparatus compels the carbonic acid evolved to pass through the sulphuric acid contained in *a* before it is permitted to escape through the tube *c*, this being the only aperture of the apparatus. It is obvious that during this transmission through sulphuric acid all the moisture with which the carbonic acid may be charged will be retained more completely than could be done in any other manner. Upon the influx of the sulphuric acid, the fluid in *b* becomes heated, and expands together with the air contained in the flask: upon cooling, both acquire their original volume again, owing to which a new portion of sulphuric acid flows over into *b* as soon as the evolution of gas has ceased: the process is, however, expedited by applying suction to the tube *c* every time the evolution of gas ceases, and in this way the operation may be accomplished in a few minutes. When the carbonate is completely decomposed (which is ascertained by no further evolution of gas taking place upon the influx of fresh portions of sulphuric acid into *b*), a somewhat larger quantity of the sulphuric acid contained in *a* is, by means of renewed suction, made to pass over into *b*: the fluid in this flask becomes hereupon heated to such an extent as to expel all the carbonic acid which it had absorbed in the course of the operation. As soon as the evolution of gas has completely ceased, the aperture of the tube *d* is opened by taking off the piece of wax, and suction applied to the tube *c*, until all the carbonic acid still contained within the apparatus is replaced by air. The apparatus is then allowed to cool, wiped dry, and weighed. The loss of weight indicates the amount of carbonic acid which was contained in the test specimen. A common apothecary's balance, that will turn with one-sixth of a grain, is sufficiently delicate for weighing not

only the whole apparatus, but the test specimen also; and it is not one of the least of the advantages of this method, that it enables the operator to experiment on a much larger scale than is possible in an ordinary analysis. Previous to submitting the sample to analysis, it must be thoroughly dried by exposure to heat over a lamp for about five minutes in a Berlin crucible, and allowed to cool with the cover on: it must also be ascertained whether any insoluble earthy carbonates are present, which is done by dissolving the specimen in water, filtering and well washing the residue: if the sample contain sulphide, sulphite, or hyposulphite of the alkali, a teaspoonful of *yellow chromate of potassa* is added to the solution in the flask, which decomposes both the sulphurous acid and the sulphuretted hydrogen at the moment of their liberation, all the products of the decomposition, viz. sulphate of chromium, water, and sulphur, remaining in the apparatus. The amount of caustic soda and potassa present in the specimen, the determination of which is of great importance, is found by comparing the quantity of carbonic acid evolved from a given weight of the alkali in its ordinary state, with that evolved from a similar quantity after it has been mixed in a moist state with carbonate of ammonia, and dried at a high temperature, by which means all the caustic alkali becomes carbonated. Should any *bicarbonates* be present, they are converted into neutral carbonates, by the application of a gentle red-heat: in order to ascertain their presence the solution to be examined is mixed with solution of chloride of calcium in excess, filtered, and ammonia added to the filtrate,—a turbidity indicates the presence of bicarbonate.

The presence of free soda in the commercial article is detected by the alkaline reaction which the solution of the sample exhibits after the addition of chloride of barium in excess. Fresenius and Will apply the same method to the analysis of carbonates, the bases of which form insoluble compounds with sulphuric acid. The apparatus is, however, somewhat modified, in order to allow of the introduction of nitric acid in the place of sulphuric acid in the bottle *b*. For this purpose the tube *d* is expanded to a bulb in its upper part, and drawn out to a fine point at its lower end; it must be adjusted into the cork of *b* in such a manner as to allow of its being raised or depressed, still, however, preserving the bottle air-tight. It is filled with dilute nitric acid, and a wax stopper having been inserted into its upper aperture it is introduced into the cork, so that its

point just reaches the surface of the water in *b*, through which the carbonate to be analysed is diffused. The nitric acid is prevented from escaping from the tube by the wax stopper. The whole apparatus is weighed, the tube *d* is then cautiously depressed, so that its point nearly reaches the bottom of the flask, and by removing the wax stopper the nitric acid gradually escapes into *b*, occasioning the decomposition of the carbonate, the liberated carbonic acid escaping through the tube *c*, and becoming deprived of moisture by the sulphuric acid in *a*, previous to escaping through *e*. When the decomposition is complete, the carbonic acid which has been absorbed by the water in *b* is expelled by plunging the apparatus into hot water, air having been previously drawn through the flasks by suction at the tube *e*. As soon as the whole is cool the flasks are wiped dry and weighed. The loss indicates the amount of carbonic acid. It is scarcely necessary to say that nitric acid is here employed, in consequence of its forming soluble compounds with the bases of such carbonates as may require to be analysed in this apparatus, viz. those of lime, strontia, and baryta.

155. Ammonium.

Ammonia is estimated as *chloride of ammonium*, and as double *chloride of platinum* and *ammonium*. It is also estimated by the volumetric process.

Quantitative estimation as Chloride.—When the alkali exists in a solution, either in an uncombined state, or as a carbonate, or combined with a weak volatile acid, or as chloride, it may be weighed in the form of the latter salt, for which purpose slight excess of hydrochloric acid is added to the solution, which is evaporated to dryness on the water bath, the residue being heated thereon till it ceases to lose weight; at this temperature the loss from volatilization is almost inappreciable. Its composition is—

One equivalent of NH_4	18·0	33·65
One equivalent of Cl	35·5	66·35
One equivalent of NH_4Cl	53·5	100·00

Quantitative estimation as double Chloride of Platinum and Ammonium.—Ammoniacal salts may be analysed by converting the ammonium into a double salt, with bichloride of platinum; for this purpose the solution is supersaturated with hydrochloric acid, and an aqueous solution of bichloride of platinum

added; the mixture is evaporated to dryness, and the residue treated precisely as the corresponding potassium salt; it is washed on a weighed filter, with alcohol, and dried at 212°; its composition is—

One equivalent of NH_4	18·00	8·07	$=7·62\ NH_3=6·278\ N$
One equivalent of Pt	98·50	44·17	
Three equivalents of Cl	106·50	47·76	
One eq. of $NH_4Cl,PtCl_2$	223·00	100·00	

When this double salt is heated to redness it is entirely decomposed, metallic platinum in a fine spongy form alone remaining; this operation may therefore be performed upon it in order to control the previous determination; the ignition must be effected carefully in a thin Berlin crucible, a gentle heat being first applied, and gradually increased until the organic matter of the filter is entirely destroyed. The crucible should be covered at first, but the cover must be removed towards the close of the operation, the crucible being then placed obliquely, in order to favour the access of air.

Ammoniacal salts may also be analysed by igniting them with a mixture of hydrate of soda and hydrate of lime;* the ammonia is liberated from its previous combination, and is received into, and condensed in hydrochloric acid; it is subsequently estimated as double chloride of platinum and ammonium, in the manner already described. The process is conducted as follows: the salt to be analysed having been thoroughly dried in the water-bath, is weighed, and intimately mixed with a sufficient quantity of soda-lime to half fill a combustion tube of hard German glass, about 14 or 16 inches long and half an inch internal diameter; in the operation of mixing, forcible pressure must be carefully avoided, or the ammoniacal salt will undergo partial decomposition, even in the cold; the combustion tube is drawn out to a point, and bent obliquely upward at its closed end: soda-lime is first introduced so as to occupy about an inch of the end of the tube, this is followed by the mixture; the remainder of the tube is filled to within an inch of the top with soda-lime that has served to rinse out

* Prepared by slaking a weighed amount of the best caustic lime, with solution of soda of such a strength that there shall be about one part of hydrated soda to two parts of anhydrous caustic lime; the mixture is heated to feeble redness in a Hessian crucible, pulverized, and kept in a well-closed phial.

the mortar, and, finally, a stopper of recently ignited asbestos is inserted; the tube is now laid in a horizontal position on the table, and a few smart taps given to it, in order to open a channel above the mixture for the passage of ammoniacal gas. The condensing apparatus, containing a small quantity of hydrochloric acid, is now attached to the tube by means of a perforated cork, the combustion tube is placed in the furnace, and the whole apparatus having been proved to be air-tight, the tube is gradually heated with red-hot charcoal, commencing at the anterior portion, and proceeding gradually towards the closed end, until the tube is red-hot throughout its whole length; when the evolution of ammonia has ceased, the point of the combustion tube is quickly broken off, and air drawn through the apparatus, so as to bring the whole of the ammonia into the hydrochloric acid. The arrangement of the apparatus is shown in Fig. 70. The only source of error to be

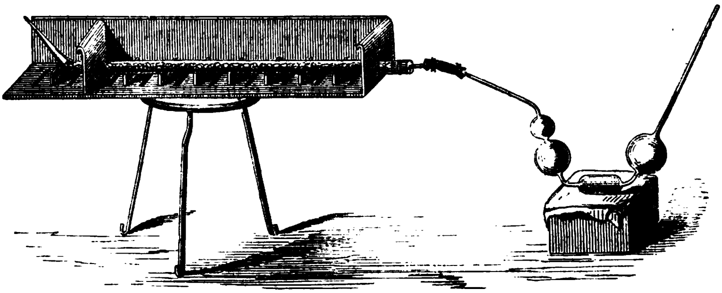


Fig. 70.

apprehended in conducting this operation arises from the powerful affinity existing between hydrochloric acid and ammonia, in consequence of which the acid is apt to rush back with violence, and enter the combustion tube, thus spoiling the whole analysis. The inventors of the method, Will and Varrentrapp, recommend mixing the substance analysed with an equal amount of sugar, which gives rise to the evolution of other and more permanent gases which serve to dilute the ammonia. The accident may be also prevented by employing a capacious condensing apparatus, and using a moderate quantity of hydrochloric acid. The operation being over, the contents of the

condensing apparatus are transferred to an evaporating basin, and the apparatus repeatedly rinsed out with water; bichloride of platinum in excess is then added, and the remainder of the process conducted as has been already directed.

Volumetric estimation of Ammonia and of Nitrogen.—Instead of weighing the ammonia condensed by the hydrochloric acid in the above process as double chloride of ammonium and platinum, it may be estimated by the method recommended by Peligot, ('Comptes Rendus,' March 29, 1847.) The bulbed receiver is partly filled with a fixed weight or volume of sulphuric acid of known strength. Now, as the ammonia which combines with the acid lowers its strength; by determining after combustion the composition of this liquid, and comparing it with that it previously possessed, it is easy to ascertain the quantity of ammonia that has been condensed; and consequently, the amount of nitrogen yielded by the substance submitted to analysis. This operation is executed with as much rapidity as precision, by means of an alkaline solution, likewise of known strength. Peligot prefers a solution of lime in syrup. By triturating slaked lime with a solution of sugar, it dissolves in far greater proportion than in pure water; and the compound formed possesses the same alkaline reaction as if the base which it contains were free. It may be preserved for a considerable time without alteration, in bottles protected from contact with the carbonic acid of the atmosphere: nevertheless, as the insoluble carbonate of lime renders the liquid turbid, it need only be filtered to serve again to determine the strength of the sulphuric acid. The operation is conducted as follows:—

A certain quantity of sulphuric acid of known strength is accurately measured into the condensing apparatus. The acid employed by Peligot contains 61·250 grammes of (HO,SO_3) to 1 litre of water; consequently, 100 cubic centimètres correspond to 2·12 grammes of ammonia, or 1·75 gramme of nitrogen.

When the combustion is finished, the acid which has served to condense the ammonia is poured into a cylindrical glass; the apparatus carefully washed, and to this liquid, diluted with much water, a few drops of litmus are added, to give it a red colour. By means of the solution of lime in sugar, which is contained in a burette graduated in cubic centimètres and in tenths of a cubic centimètre, the acid liquid is accurately saturated, the operator being guided by the blue colour which the

liquor suddenly acquires when the point of saturation is attained. The quantity of alkaline liquor required to produce this effect is read off on the burette; and as the amount of the lime compound which saturates 10 cubic centimètres of the normal solution of sulphuric acid has been determined by a previous experiment; by subtracting from this quantity, that found for the acid which has absorbed the ammonia from the nitrogenous substance, we find the volume of the acid solution which has been saturated by the ammonia, and, consequently, the weight of the nitrogen which the body contained.

Schlæsing's method of determining the amount of Ammonia when accompanied by nitrogenous substances. (Ann. de Chim., February, 1851.)

A known weight of the substance is dissolved in water and placed in a shallow vessel, over which is supported, on a glass tripod, a shallow saucer containing sulphuric acid of known strength. The ammoniacal solution is mixed with caustic potassa or with milk of lime, and covered with a bell glass, the edges of which rest on mercury contained in a large shallow dish. After a period varying from 24 to 28 hours, according to the bulk of the ammoniacal solution, the whole of the ammonia is disengaged and is absorbed by the sulphuric acid, the strength of which is again determined by means of saccharate of lime according to Peligot's method. This process does not answer so well with insoluble salts of ammonia, which the author directs to be dissolved in nitric acid; the operation then goes on very slowly, requiring sometimes 72 hours for the complete absorption.

Walker (Chem. News, Nov. 24, 1860) condenses the ammonia produced by the decomposition of nitrogenous organic substances, manures, etc., by igniting them with soda-lime, in a dilute solution of *chloride of zinc* (sp. gr. 1·025) using about *ten* fluid ounces for each analysis; *oxide of zinc* is precipitated, every 40 parts of which correspond to 17 of ammonia. The results he states to be very accurate.

For determining the amount of ammonia in rain-water, Boussingault submits to distillation 1 litre (about 35$\frac{1}{4}$ oz.) of water, to which a little caustic potassa has been added, and collects and tests by the alkalimetrical method two or more successive fifths or tenths of the products. For this purpose he uses a test acid only $\frac{1}{40}$th of the strength of that employed by Peligot, and a test alkaline solution not quite a third of the strength,

volume for volume, of this test acid. In practice Boussingault finds that the limit of error in the use of this dilute alkaline solution is about 0·2 cub. cent. measures of it, equal to about 0·033 milligramme, equal to 0·0005 grain of ammonia. Messrs. Lawes and Gilbert operate upon several litres of water in the first instance, reducing the bulk by successive distillations to one-half; it is thus brought to a convenient amount for final distillation and subsequent testing of measured proportional amounts of the distillate, according to Boussingault's method.

The amount of ammonia in manures, the ammoniacal liquor of gas-works, etc., may be determined by distilling known weights or volumes in a flask, into which caustic potassa is allowed to flow from a suitable apparatus furnished with a clip, the product being received in another large flask containing a known volume of normal acid, the strength of which after the operation, is again tested in the usual manner. The distillation should be conducted cautiously, and the flask should be sufficiently large to prevent the liquid from frothing over; the end of the delivery tube should be cut slanting, and just reach the surface of the acid in the receiver; the boiling should continue for fifteen or twenty minutes.

Separation of Ammonia from Potassa and Soda.—When all three alkalies are present in combination with the same volatile acid, the ammoniacal salt may be expelled from a weighed portion of the mixture by careful ignition, and the amount of ammonia calculated from the loss of weight. If the mixture contain ammonia in the form of chloride or carbonate, it may likewise be expelled by heat from the salts of the other alkalies, but if the ammonia be present in combination with a non-volatile acid, or if the mixture cannot be dried at a temperature insufficient to expel ammonia, it must be determined by combustion with soda lime, and the other alkalies must be estimated from a separate portion, which has been previously gently ignited it to expel all the ammonia. If no potassa be present, ammonia may be separated from soda by bichloride of platinum.

GROUP II.

The Metals of the Alkaline Earths:—Barium, Strontium, Calcium, Magnesium.

156. Barium.

Oxide of Barium, or *Baryta*, is weighed as *carbonate* and as *sulphate*, most frequently as the latter, which is completely insoluble in water, and extremely sparingly so in all acids.

Quantitative estimation as Sulphate.—To the solution containing the earth, heated to 212°, dilute sulphuric acid is added in excess; the fluid is well agitated, poured into a beaker, and allowed to stand till the precipitate has settled, and the supernatant fluid become quite clear: it is then transferred to a filter, the amount of ash yielded by which is known, and washed with hot distilled water until the wash-water no longer produces any precipitate with chloride of barium, it is then dried and ignited, the heat being continued until the organic matter of filter is completely destroyed, and the contents of the crucible perfectly white; when quite cold, it is weighed. Its composition is—

One equivalent of BaO	76·5	65·66
One ditto of SO_3	40·0	34·34
One ditto of BaO,SO_3	116·5	100·00

Quantitative determination as Carbonate.—In certain cases the precipitation of baryta by sulphuric acid is inadmissible; it is then thrown down in the form of carbonate, by carbonate of ammonia, mixed with a little caustic ammonia; the precipitate is allowed to settle in a warm place, and is washed on the filter with water, rendered slightly alkaline by ammonia. It may be heated to redness, without losing carbonic acid.

Its composition is—

One equivalent of BaO	76·5	77·66
One ditto of CO_2	22·0	22·34
One ditto of BaO,CO_2	98·5	100·00

Baryta is estimated as *carbonate* when it exists in combination with an organic acid: the salt is carefully ignited in a platinum crucible, first covered, and afterwards, with free access of air; the heat is continued till the residue is perfectly white; it is then allowed to cool, moistened with carbonate of ammonia, and again gently ignited.

Separation of Baryta from the Alkalies.—The compound is dissolved in water or in hydrochloric acid, if necessary; the baryta is precipitated as *sulphate*, the alkalies being in this case obtained also in the state of sulphates by evaporating the filtered solution; or as *carbonate*, in which case the alkalies may be obtained as chlorides, which is the most convenient form if they have subsequently to be separated from each other.

157. Strontium.

Oxide of Strontium or *Strontia* is also weighed as *sulphate* and as *carbonate;* it is precipitated in the form of both salts precisely as baryta; but, as sulphate of strontia is not altogether insoluble in water, spirits of wine are added to the fluid, to diminish its solubility: when this is inadmissible, it is better to precipitate the earth as carbonate, washing the salt on the filter with water containing ammonia and carbonate of ammonia.

The composition of sulphate of strontia is—

One equivalent of SrO . . .	51·75 . .	56·44
One ditto of SO_3 . . .	40·00 . .	43·56
One ditto of SrO,SO_3 ·	91·75	100·00

The composition of carbonate of strontia is—

One equivalent of SrO . .	51·75 . .	70·20
One ditto of CO_2 . . .	22·00 . .	29·80
One ditto of SrO,CO_2 .	73·75 . .	100·00

Separation of Strontia from Baryta.—The hydrochloric solution of the earths is mixed with excess of hydrofluosilicic acid, and allowed to remain at rest for some hours: the crystalline precipitate of silico-fluoride of barium is collected on a weighed filter, washed and dried at 212°: the strontia in the filtrate is estimated either as sulphate or as carbonate.

The composition of silico-fluoride of barium is

One equivalent of Ba . .	68·5 .	49·50 = 54·84 BaO
One ditto of Si . .	14·0 .	10·63
Three ditto of F . .	57·0 .	40·87
One ditto of BaF,SiF_2 .	139·5	100·00*

* According to Rose (Pogg. Ann., Nov. 6, 1850), silico-fluoride of barium is not entirely insoluble in water, and therefore perfectly accurate results are only obtained when the precipitation is effected from a spirituous solution. A small quantity of alcohol need only be added to render the precipitation complete.

Separation of Strontia from the Alkalies.—This is effected in the same manner as the separation of baryta.

158. Calcium.

Oxide of Calcium, or *Lime*, is estimated as *sulphate* and as *carbonate*. As sulphate of lime is soluble to a considerable extent in water, it is necessary to add to the solution about to be precipitated by sulphuric acid, twice its volume of alcohol, and to wash the sulphate of lime on the filter with spirit: it is ignited previous to weighing.

The composition of sulphate of lime is—

One equivalent of CaO	. .	28	. . 41·17
One ditto of SO_3	. . .	40	. . 58·83
One ditto of CaO,SO_3	. .	68	. . 100·00

Quantitative determination as Carbonate.—If the lime salt be soluble in water, and if the solution be perfectly neutral, oxalate of ammonia is added as long as a precipitate is produced; the oxalate of lime is allowed to settle completely, which usually requires some hours, the vessel (a beaker, or a Phillips's precipitating-jar) being covered, and placed in a warm situation; it is then filtered, and the salt, having been thoroughly washed with hot water, is dried and exposed to a dull red-heat for twenty minutes; the oxalate of lime is by this means converted into carbonate; but, as it is possible that it may have lost carbonic acid during ignition, it is safer, before weighing, to moisten it with a few drops of solution o carbonate of ammonia, to evaporate to dryness on the water-bath, and again expose it to a very gentle ignition.

The composition of carbonate of lime is—

One equivalent of CaO	. . .	28	. . 56
One ditto of CO_2	. . .	22	. . 44
One ditto of CaO,CO_2	. .	50	. . 100

If, however, the lime salt can only be held in solution by a free mineral acid, or if it will not bear the addition of excess of ammonia without a precipitation taking place, as is the case with *phosphate of lime* for example, the lime is best estimated as sulphate, because, oxalate of lime being soluble in mineral acids, it would be impossible to precipitate it from a solution containing free nitric or hydrochloric acid; oxalate of lime is, however, insoluble, or nearly so in *acetic acid*, and like-

wise in *oxalic acid.* Very accurate results may therefore be obtained by adding to the hydrochloric solution of the lime salt sufficient ammonia to occasion a slight precipitate, then a drop or two of hydrochloric acid to redissolve this precipitate, then oxalate of ammonia in excess, and finally, *acetate of potassa,* a portion of which becomes decomposed by the free hydrochloric acid, liberating a corresponding quantity of *acetic* or *oxalic* acid, in which, as before observed, oxalate of lime is almost entirely insoluble.

Separation of Lime from Baryta, Strontia, and the Alkalies.

(a.) *From Baryta.*—This is best effected by adding to the acid solution of the two earths very diluted sulphuric acid, as long as precipitation occurs; if the sulphuric acid be sufficiently diluted, no lime will be precipitated.

(b.) *From Strontia.*—This is effected with some difficulty; the only good method is that recommended by Stromeyer, which is based on the complete solubility of nitrate of lime in absolute alcohol, and the insolubility of nitrate of strontia in the same menstruum. The two earths are converted into nitrates, excess of nitric acid being carefully avoided, the solution is evaporated to dryness in a flask that can be closed, and the residue digested for several hours with absolute alcohol, being frequently shaken; the mixture is then filtered, and the undissolved residue washed with alcohol; both earths are then estimated as sulphates.

(c.) *From Baryta and Strontia.*—When all three earths are together in a solution, the baryta is first precipitated by hydrofluosilicic acid; the lime and the strontia are obtained from the solution filtered from the silico-fluoride of barium in the form of sulphates, by the addition of sulphuric acid and evaporation to dryness; the mixed sulphates are fused in a platinum crucible with three times their weight of mixed carbonates of potassa and soda; the fused mass is extracted with water, and the earths are thus obtained in the state of carbonates. They are next converted into nitrates, and separated by alcohol, as above directed.

(d.) *From the Alkalies.*—The process for effecting this is very simple; the lime is separated by oxalate of ammonia, with the usual precautions; the filtered solution is evaporated to dryness, and ignited to expel the ammoniacal salts; the residue is dissolved in water, and the alkalies determined according to the method already described.

159. Magnesium.

Oxide of Magnesium, or *Magnesia*, is weighed as *sulphate*, or as *pyrophosphate*, and sometimes as pure *magnesia*.

Quantitative estimation as Sulphate.—The earth is determined in the form of this salt when no other fixed constituent is present; the solution containing it, is mixed with excess of sulphuric acid, evaporated to dryness, and ignited in a platinum crucible; the residue is again treated with dilute sulphuric acid, evaporated to dryness, and again gently ignited; the residue is pure anhydrous sulphate of magnesia, the composition of which is—

One equivalent of MgO	20·16	33·51
One ditto of SO_3	40·00	66·49
One ditto of MgO,SO_3	60·16	100·00

Quantitative estimation as Pyrophosphate.—Chloride of ammonium is added to the solution, then ammonia in excess; should a precipitate hereupon occur, a fresh quantity of chloride of ammonium is added, by which the precipitate is redissolved; solution of phosphate of soda is then dropped into the mixture as long as precipitation takes place. The whole is well agitated, and allowed to repose for several hours: the precipitate is collected on a filter, the amount of ash furnished by which is known, and washed with water containing about one-eighth of ammonia, in which the *basic phosphate of magnesia* and *ammonia* ($2MgO,NH_4O,PO_5 + 24aq.$), is scarcely sensibly soluble; the washed salt is dried, and carefully ignited, together with the filter; the latter requires considerable time for incineration, which is best effected by cutting in strips and burning it on the lid of the crucible. The composition of the ignited salt is—

Two equivalents of MgO	40·32	36·22
One equivalent of PO_5	71·00	63·78
One ditto of $2MgO,PO_5$	111·32	100·00

Separation of Magnesia from Baryta, Strontia, Lime, and the Alkalies:—

(a.) *From Baryta and Strontia.*—The two latter earths are precipitated by carbonate of ammonia, a sufficient quantity of chloride of ammonium having previously been added to the solution to prevent the precipitation of the magnesia: the pre-

cipitated carbonates of baryta and strontia are dissolved in hydrochloric acid, and the baryta separated from the strontia by hydrofluo-silicic acid; the magnesia is determined in the filtrate as pyrophosphate; if no strontia be present, the baryta may be precipitated as sulphate.

(b.) *From Lime.*—There are several methods of effecting this. 1st, by *oxalate of ammonia:* Chloride of ammonium is added to the solution of the two earths, then slight excess of ammonia; the lime is then precipitated by oxalate of ammonia, with the proper precautions, and the magnesia in the filtrate determined as pyrophosphate. 2nd, by *sulphate of lime:* For this purpose the two earths must be in the state of sulphates; the mixture having been ignited, is digested with a saturated solution of sulphate of lime, and the insoluble residue washed on a filter with the same salt; the whole of the sulphate of magnesia is thus removed, the sulphate of lime, being quite insoluble in a saturated solution of sulphate of lime, remaining on the filter; it is heated to redness and weighed, and from the difference in weight, before and after the operation, the amount of sulphate of magnesia is calculated. 3rd, by *chlorate of potassa:* The hydrochloric solution of the two earths is evaporated to dryness, and ignited in a platinum crucible, chlorate of potassa is then added in small quantities at a time, until the evolution of chlorine ceases. The mass on cooling is extracted with water, which dissolves the chloride of calcium, and leaves a residuum of pure magnesia, the chloride of magnesium having, under the influence of heat, aided by the chlorate of potassa, been completely decomposed: the lime is determined in the aqueous solution by oxalate of ammonia.

(c.) *From the Alkalies:*—

I. *Berzelius's method.*—The bases are brought to the state of chlorides, to a concentrated solution of which, finely powdered and perfectly pure red oxide of mercury is added in excess; mutual decomposition of the chloride of magnesium and of the oxide of mercury takes place, *chloride of mercury* being formed, which combines with the alkaline chlorides, forming a soluble double salt, and *magnesia*, which remains undissolved, on extracting the evaporated and ignited mass with water. The solution, filtered from the magnesia, is evaporated to dryness, and heated, to expel the chloride of mercury: the alkaline chlorides alone remain, which are separated from each other as directed (page 259); the *magnesia* may be contaminated with

undecomposed oxide of mercury, from which, however, it is readily freed by heat. This method is well adapted for the the analysis of *mineral waters*, *soils*, etc.

II. *Liebig's method.*—This also gives accurate results; baryta-water is added to the hydrochloric solution to alkaline reaction, magnesia is thereby precipitated, *baryta* being a stronger base than *magnesia*, in consequence of which it deprives it of its electro-negative element; to the solution, filtered from the precipitated magnesia, carbonate of ammonia, mixed with caustic ammonia, is added, the excess of baryta is thereby removed, and is filtered off; the alkalies are contained in the filtrate in the form of chlorides, and are separated from each other in the usual manner.

III. *Sonneschein's method* (Poggendorff's 'Annalen,' 74, p. 313).—The compounds to be separated are converted in the usual manner into chlorides, which are evaporated to dryness, and then heated to faint redness, when any ammoniacal salt contained in the solution, as well as a portion of the hydrochloric acid combined with the magnesium, escapes. When the dry mass is cool, water is poured over it, it is then boiled with *carbonate of silver* until the liquid has a strong alkaline reaction. The boiling is continued for about ten minutes, stirring the whole time, when the decomposition is complete. The solution is then filtered as hot as possible, and the precipitate washed with hot water. The filtered liquid now contains only the alkalies, and a trace of the silver salt, which is removed by hydrochloric acid, and the alkalies are then determined in the usual manner. The residue left upon the filter is digested with hydrochloric acid, and, after removing the chloride of silver, the magnesia is precipitated in the usual manner with phosphate of soda and ammonia. The carbonate of silver is best prepared by carefully precipitating nitrate of silver with carbonate of ammonia; after subsidence, the precipitate is easily freed from the ammoniacal salt by the frequent addition of water, and decantation. It is not necessary to filter it, as the moist precipitate is more easily decomposed.

IV. *Heintz's method* (Poggendorff's 'Annalen,' 73, p. 119).—The solution containing the three bases is supersaturated with ammonia, and if it contain no chlorides a few drops of chloride of ammonium are added. Should a troubled appearance arise in the liquid, it is treated with solution of chloride of ammonium until this vanishes. The magnesia is then precipi-

tated by phosphate of ammonia, the precipitate washed with ammoniacal water, dried, heated to redness, and weighed. The free ammonia in the filtrate having been partly removed by boiling, the phosphoric acid is precipitated at the boiling temperature by nitrate or acetate of lead. When an excess of the lead salt has been used, a solution of carbonate of ammonia, containing free ammonia, is added to the hot liquid, which is then allowed to stand for a few minutes; it is subsequently filtered, and the amount of potash and soda contained in the filtrate is ascertained by the usual methods. It is essential that some chloride should be present in the solution in order that a compound of chloride and phosphate of lead may be produced, from which ammonia cannot extract any phosphoric acid.

v. *Watts's method.*—This consists in precipitating the magnesia by a known weight of carbonate of soda, using considerable excess, then boiling and filtering, treating the filtrate with a slight excess of acid, evaporating to dryness, and igniting the residue to render it neutral, weighing the neutral salt thus obtained, and making the proper correction for the quantity of soda-salt introduced. To ensure accuracy, the solution, after the addition of the carbonate of soda, must be well boiled for at least half an hour, in order to decompose a difficultly soluble double carbonate of soda and magnesia, which is formed on the first addition of the alkaline carbonate. The carbonate of soda must likewise be added in considerable excess, otherwise the precipitation will not be complete. The precipitate of carbonate of magnesia must be washed with boiling water, and the washing not too long continued, the carbonate not being completely insoluble. The washing should be discontinued as soon as the wash-water ceases to give a distinct alkaline reaction: when this takes place, the water begins to dissolve the carbonate of magnesia. (Quart. Journ. Chem. Soc.)

vi. *Ebelmen's method.*—To the solution of the mixed sulphates, recently prepared carbonate of baryta is added, and then a stream of carbonic acid passed through the liquid till it contains a portion of the baryta in solution in the form of bicarbonate, which period is known by filtering a few drops of the liquid, and adding one drop of exceedingly dilute sulphuric acid, if a cloudiness is produced, the liquid can contain no sulphate in solution. It is then filtered, and the filtrate evaporated to dryness at a pretty high temperature, in order to reduce the

whole to the state of neutral carbonates; the residue is treated with a small quantity of boiling water, which dissolves only the alkaline carbonates. (Ann. de Chim. et Phys. Nov. 1859.)

VII. *Reynoso's method.* ('Comptes Rendus,' lvi. No. 18.)—From the liquid acidulated with nitric acid, the lime (if present) is precipitated by the addition of ammonia and oxalate of ammonia. To the filtered liquid, phosphate of ammonia or phosphoric acid alone is added, and the ammonio-magnesian phosphate collected. The filtrate is evaporated to dryness and calcined to get rid of the ammoniacal salts, and the potassa and soda remain united with phosphoric acid only. To ensure accuracy, the calcined residue should be again treated with nitric acid and again evaporated to dryness and ignited; it is then treated in a flask with a large excess of *tin* and nitric acid; the phosphoric acid is hereby eliminated; it is filtered, and the filtrate concentrated; the residuum composed of nitrates of potassa and soda is calcined till completely decomposed, and as soon as the capsule is cold, the caustic alkalies are weighed, or transformed into carbonates, after which they are converted into chlorides and separated by bichloride of platinum.

GROUP III.

Aluminum, Glucinum, Yttrium, Thorinum, Zirconium, Chromium.

160. Aluminum.

Sesquioxide of Aluminum, or *Alumina*, is precipitated from its solutions by ammonia, or carbonate of ammonia, chloride of ammonium having been previously added and heat applied. The precipitate, which is very bulky, requires long-continued washing with hot water; its ignition must be carefully performed in order to avoid loss by spirting. It shrinks very much in drying. Its composition is—

Two equivalents of Al	27·4	53·32
Three ditto of O	24·0	46·68
One ditto of Al_2O_3	51·4	100·00

It is never weighed in any other form, than as pure alumina. The washing of precipitated alumina is greatly facilitated by allowing it to dry slightly on the filter before commencing washing.

Separation of Alumina from the Alkaline Earths and Alkalies.—To the hydrochloric solution of the mixture, chloride of ammonium is added, then ammonia quite free from carbonic acid; the alumina is precipitated, carrying with it a little magnesia; it must be separated by filtration as rapidly as possible, the funnel being covered with a glass plate to prevent the access of carbonic acid, which would determine the precipitation of the earthy carbonates; the precipitate on the filter is well washed with hot water, it is then, while still moist, dissolved in hydrochloric acid, and boiled with excess of pure potassa; the small quantity of magnesia remains undissolved, and, having been separated from the alkaline ley by filtration, it is well washed, dissolved in a small quantity of hydrochloric acid, and added to the solution containing the alkaline earths and the rest of the magnesia. The potassa ley contains the whole of the alumina, which is precipitated by adding excess of hydrochloric acid, and, finally, supersaturating with ammonia; the alkaline earths and alkalies are separated from each other in the manner directed in the last section. The success of this process depends on the freedom of the ammonia from carbonic acid, and on the rapid filtering and careful washing of the precipitated alumina. If alumina has to be separated from baryta only, the latter earth may effectually be removed by sulphuric acid.

Separation of Alumina from Lime only.—The alumina is precipitated by ammonia free from carbonic acid, with the precautions just prescribed; and the lime in the filtrate is precipitated by oxalate of ammonia.

Separation of Alumina from Magnesia alone.—This may be effected by either of the following methods:—If the quantity of magnesia be small, the mixture of the two earths may be dissolved in hydrochloric acid, excess being avoided, and the solution boiled with excess of caustic potassa, by which the alumina is dissolved, magnesia remaining behind. If the quantity of magnesia be considerable, chloride of ammonium is added to the hydrochloric solution of the two earths, and the alumina is precipitated by ammonia; but, as it carries with it a small quantity of magnesia, it must be redissolved in hydrochloric acid and treated with caustic potassa as above; it is not safe to treat at once the hydrochloric solution of the earths with excess of caustic potassa when the quantity of magnesia is considerable, it being in this case very difficult to separate them by an alkaline ley. The best method

of separating *alumina* from *magnesia* is probably to precipitate the former by bicarbonate of potassa, and to estimate the magnesia in the filtrate as *pyrophosphate of magnesia;* the alumina precipitated in this manner carries with it a portion of potassa, which it is almost impossible to remove by washing; it must therefore be redissolved in hydrochloric acid and reprecipitated by carbonate of ammonia.

Separation of Alumina from Lime and Magnesia. (Rose).—Instead of being careful to employ ammonia free from carbonic acid and avoiding the presence of this gas, the liquid in which the alumina has been precipitated by excess of ammonia is heated to ebullition. When the evolution of ammonia ceases, all the alumina is in the precipitate, and may be separated by filtration without requiring any special precaution, for the simple reason that in the presence of ammoniacal salts the carbonate of lime is decomposed, the lime entering into solution; a little chloride of ammonium may be added if there is a chance of there not being sufficient to favour this decomposition. When the lime is present in small quantities only, tartaric acid may be added, and the solution then supersaturated with ammonia. The lime is precipitated in the form of tartrate if there be only a little alumina present, otherwise it remains in solution, but can be perfectly separated in the form of oxalate. When *magnesia* is present, the tartaric acid process may also be used, the lime being precipitated first by oxalic acid, and then the magnesia in the state of ammonio-magnesian phosphate, but traces of alumina are carried down with the magnesia.

161. Glucinum.

Oxide of Glucinum, or *Glucina*, like *alumina*, is only weighed in its pure form, as precipitated from its solution by *caustic* ammonia. Its composition is—

One equivalent of Gl . . .	4·66 . .	36·9
One ditto of O	8·0 . .	63·1
One ditto of GlO	12·66 . .	100·0

Separation of Glucina from Alumina.—Three methods have been proposed. The *first* depends on the solubility of *glucina* in carbonate of ammonia, and the insolubility of *alumina* in that reagent. The solution containing the two earths is mixed in a flask with a very considerable excess of a concentrated so-

lution of carbonate of ammonia, the flask is closed, and occasionally shaken; when it is observed that the precipitate ceases to diminish in bulk, the *alumina* is separated by filtration, and the filtrate evaporated to dryness, and ignited, to expel the ammoniacal salts; the residue, provided no other base or fixed acid be present, is pure *glucina:* or both the earths may be together precipitated by ammonia, and the precipitate digested with carbonate of ammonia till the glucina is entirely dissolved.

The *second* method is to dissolve both earths in a hot and concentrated solution of caustic potassa, to allow the ley to cool, and then to dilute it considerably with water, and again boil; the *glucina* is in this manner precipitated, while the *alumina* remains in solution.

The *third* method is that proposed by Berthier. The earths are dissolved in sulphuric acid, the solution concentrated, and sulphate of ammonia added, which causes the separation of the greater portion of the alumina in the form of an *alum:* to the decanted and diluted liquid, *sulphite* of ammonia is added, and it is boiled until sulphurous acid ceases to be liberated; the alumina is entirely precipitated, and the glucina remains in solution, and may afterwards be precipitated by ammonia: or both earths may be together precipitated by ammonia, and, while moist, treated with sulphurous acid, which redissolves both, but on boiling the solution, the alumina is completely precipitated.

The separation of glucina from *lime*, *magnesia*, and the *alkalies*, is effected in the same manner as the separation of alumina.

162. Yttrium.

Oxide of Yttrium, or *Yttria*, is weighed as the pure earth, in which state it is precipitated by caustic alkalies; it must, however, be observed, that when it is dissolved in nitric or sulphuric acid, *potassa* must be the precipitant employed; in the latter case it is, according to Wöhler, almost impossible to procure it free from sulphate of potassa. Its composition is—

One equivalent of Y	32 . .	80·0
One ditto of O	8 . .	20·0
One ditto of YO	40 . .	100·0

Separation of Yttria from Alumina and Glucina.—This is easily accomplished by digesting the mixture of the three earths in caustic potassa in which *yttria* is insoluble.

Separation of Yttria from Magnesia and the Alkalies.—From magnesia, yttria is separated by caustic ammonia, chloride of ammonium having been previously added to the solution; from the alkalies it is separated precisely in the same manner as alumina.

163. Thorinum.

Of *Oxide of Thorinum*, or *Thorina*, little is known: from *alumina* it is distinguished by its insolubility in caustic potassa, and as it is completely precipitated from its solutions by ammonia, even in the presence of chloride of ammonium, it may thus be separated from *magnesia* and *lime*. *Thorina* forms, with sulphate of potassa a double salt, quite insoluble in sulphate of potassa; this salt may, therefore, be employed to separate it from most other substances, but it must be concentrated and in excess; the double salt, after being washed, is dissolved in boiling water, and the *thorina* precipitated by caustic potassa. Its composition is—

One equivalent of Th . . .	59·5 . .	88·15
One ditto of O	8·0 . .	11·85
One ditto of Th O	67·5 . .	100·00

164. Zirconium.

Oxide of Zirconium, or *Zirconia*, is precipitated from its solution by *ammonia* and by *caustic potassa;* the latter is the best precipitant, the former often throwing down subsalts instead of the pure earth. Sulphate of potassa added in crystals and in sufficient quantity to saturate the liquid, which must be first completely neutralized by potassa, throws down the whole of the earth in the form of a double salt; it must be washed with water containing ammonia, and then boiled with caustic potassa, which leaves hydrate of *zirconia* in a pure state. Its composition is—

One equivalent of Zr .	44·75 . . .	73·66
Two equivalents of O . .	16·00 . . .	26·34
One equivalent of ZrO_2	60·75 . . .	100·00

The solubility of *zirconia* in bicarbonate of potassa affords a means of separating it from *alumina*, but an accurate method of separating it from *yttria* and *glucina* remains to be discovered.

165. Chromium.

Sesquioxide of Chromium is usually estimated quantitatively in its pure state; the solution containing it, is heated to the boiling temperature, and, ammonia being added in slight excess, it is boiled for about half an hour, or until the solution is perfectly colourless; the precipitate is collected on a filter, washed with boiling water, dried, and ignited. Its composition is

Two equivalents of Cr	52·6	68·67
Three ditto of O	24·0	31·33
One equivalent of Cr_2O_3	76·6	100·00

The ignition of this oxide must be performed with care, as at a particular temperature it suddenly becomes incandescent with a sort of explosion, whereby a portion may be projected from the crucible. The crucible should be closed with its cover.

When chromium exists in a solution in the form of chromic acid, it may be estimated as chromate of baryta or as chromate of lead, by adding respectively nitrate of baryta or nitrate of lead to the solution; it may also be precipitated by subnitrate of mercury, the resulting chromate being decomposed by ignition into mercury, oxygen, and oxide of chromium; from the weight of the latter the quantity of chromic acid may be calculated; it is better, however, to reduce the chromic acid to oxide of chromium in the solution previous to precipitating it, which is done by concentrating the solution and boiling it with excess of hydrochloric acid, mixed with alcohol, till the liquid assumes a pure green colour. The reduced oxide of chromium is precipitated by ammonia, after the excess of alcohol has been expelled by a gentle heat.

Estimation of Chromium in its compounds:—

1. *Vohl's method* (Liebig's 'Annalen,' Sept. 1847.)—This method is applicable to the determination of the metal, whether occurring in the form of oxide, or as chromic acid, but when the metal exists as oxide of chromium, it must in the first place be converted into chromic acid. The process depends on the conversion of oxalic into carbonic acid, by the oxygen furnished by the reduction of chromic acid into oxide of chromium; thus—

$$2(CrO_3) + 3(C_2O_3) = Cr_2O_3 + 6CO_2$$

For each equivalent of chromic acid, three equivalents of carbonic acid are formed, or 66 parts by weight for 50·3 parts of chromic acid. To determine the amount of carbonic acid, the

author employs the alkalimetrical apparatus of Fresenius and Will (page 268). If merely the chromium has to be determined, any oxalate may be taken, but, if the alkalies are to be determined in the residuary liquid, oxalate of ammonia or baryta is employed. The analysis is very simple: when the chromium exists in the compound in the form of acid, the salt is taken just as it is, and the process is precisely the same as in the analysis of manganese ores (to be described further on). If the salt is a chloro-chromate, before allowing the sulphuric acid to pass over, oxide of mercury must be mixed with the salt, to prevent the elimination of chlorine or hydrochloric acid: after the operation, the amount of chlorine can be determined from the chloride of mercury by nitrate of silver, and the quantity of chloro-chromic acid contained in the salt calculated from it.

The determination is less simple when the salt contains oxide of chromium. In the first place, the oxide must be converted into chromic acid, and this is best effected in the following manner:—The salt to be examined is dissolved in water, and caustic potassa added to it until the whole of the hydrated oxide of chromium has redissolved; upon which, keeping the solution cold, chlorine is passed into it until the green colour is changed into a yellowish-red one: an excess of potassa is now added to this liquid, which is evaporated in the water-bath, and heated to faint redness in a platinum crucible. The whole of the chlorate of potassa is decomposed, chromate of potassa and chloride of potassium remaining; these are dissolved, transferred with oxide of mercury into the apparatus, and the operation conducted as with chromates. The amount of oxide of chromium can be easily calculated from the quantity of carbonic acid which has escaped; 6 equivalents of carbonic acid are set free for each equivalent of oxide of chromium:—

$$Cr_2O_3 + O_3 = 2CrO_3$$
$$2(CrO_3) + 3(C_2O_3) = Cr_2O_3 + 6CO_2$$

In analysing a salt in which both chromic acid and oxide of chromium occur, two determinations must be made. In the first place, the carbonic acid which the salt yields as it is, is determined, and the chromic acid calculated from the amount; upon which the liquid is treated as a salt of the oxide, the quantity of carbonic acid first obtained subtracted from that last obtained, and the amount of oxide of chromium calculated from the difference.

This method will, according to M. Vohl, render it possible

for every one to submit to analysis those compounds of chromium which occur so frequently adulterated in commerce.

II. *Bunsen's method.*—When a chromate, e.g. bichromate of potassa, is boiled with excess of fuming hydrochloric acid, every 2 at. of chromic acid eliminate 3 at. of chlorine:—

$$KO,2CrO_3 + 7HCl = Cr_2Cl_3 + 7HO + KCl + Cl_3.$$

The decomposition is rapid and complete, and on it Bunsen has founded a volumetric process for analysing chromates. The decomposition of the salt is effected in a small flask, having a gas delivery tube, which conducts the evolved chlorine into a solution of iodide of potassium, 3 equivalents of iodine are set free, which are estimated by means of a standard solution of sulphurous acid. ('Journal of the Chemical Society,' vol. viii. p. 227.)

III. *Schwartz's method.*—The whole of the chromium is converted into chromic acid, and when oxide of chromium is present it is oxidized by fusion with hydrate and chlorate of potash. The chromic acid is then reduced to sesquioxide of chromium by a known quantity of protoxide of iron; the quantity which remains unoxidized after the operation being determined according to Marguerite's method (see IRON) by a standard solution of permanganate of potassa; the difference between the protoxide of iron left, and that consumed, gives the amount of protoxide oxidized by the chromic acid, thus—

$$6FeO + 2CrO_3 = 3Fe_2O_3 + CrO_3.$$

From this formula the quantities of chromium, sesquioxide of chromium and chromic acid may be determined: 1·000 iron corresponds to 0·3143 chromium, to 0·4571 sesquioxide, and to 0·600 chromic acid.

Analysis of Chrome Ores.—Eight or ten grains of the ore reduced to an impalpable powder are put into a platinum crucible, and covered with ten or twelve times the weight of bisulphate of potassa; the crucible is carefully heated for about fifteen minutes to about the temperature of the fusing-point of the bisulphate, then raised to low redness, at which temperature it is kept for another quarter of an hour; the mass enters into quiet fusion, and vapours of sulphuric acid are evolved freely. The temperature is gradually raised until the whole is in perfect fusion. To the fused mass about 50 grains of pure carbonate of soda are added, and the mixture is again fused at as low a temperature as possible, pure nitre being added by degrees in quantity equal to that of the carbonate of soda.

The crucible is kept at a low red-heat for about an hour, and then raised to a bright red-heat, at which it is kept for a quarter of an hour longer. When cold the fused mass is dissolved in boiling water, filtered whilst boiling hot, and the residue on the filter washed with boiling water. If this residue should contain any undecomposed ore, it must be again fused as before with bisulphate of potash, carbonate of soda, and nitre. The filtrate contains the whole of the *chromium* as *chromate of potash*, together with small quantities of *silicic acid*, *alumina*, and sometimes *titanic* and *manganic acids*. Excess of nitrate of ammonia is added, and the solution is evaporated nearly to dryness on the water-bath, until all the liberated ammonia has been expelled, water is now added, and the precipitate, if any, is filtered off: the filtrate is made strongly acid with *sulphurous acid*, carefully heated to boiling, precipitated with slight excess of ammonia boiled for a few minutes and filtered. The thorough washing of the chromic oxide is not easy. Genth (Chem. News, No. 137) finds it succeed best in the following way:—After the precipitate has settled, the clear liquid is passed through the filter, then boiling water is added to the precipitate, and after settling, the supernatant liquid is filtered, the precipitate is then thrown on the filter, and washed twice or three times with boiling water; it is then washed back again into the dish, and boiled with water, until the little lumps which clog together are completely broken up; it is then filtered, and this operation is repeated until the wash-waters do not show the presence of any sulphates by chloride of barium. The precipitate is then dried and burned, after which it is again boiled with water to which a few drops of sulphurous acid have been added, then ammonia added, and the precipitate washed, dried, ignited, and weighed. By this mode of analysis, Dr. Genth states that the chromic oxide is obtained quite pure, and that two analyses of the same sample will not, if the process be carefully conducted, vary more than 0·25 per cent.

Separation of Oxide of Chromium from Alumina, the Alkaline Earths, and the Alkalies:—

(a.) *From Alumina.*—The usual method is to fuse the mixture of the two oxides with twice its weight of carbonate of soda, and twice and a half of its weight of nitre, the oxide of chromium becomes converted into alkaline chromate, which is extracted with water, and the alumina which remains undissolved is freed from alkali by dissolving in hydrochloric acid, and precipitating by

ammonia. According to Dr. Schaffhaeutl, however, a portion of alumina in this process always dissolves along with the alkaline chromate; he therefore recommends to convey the precipitate obtained by adding ammonia to the solution containing the two oxides into a hot concentrated solution of caustic potassa, and to boil the whole down till near solidification; when quite cold, water is added, and the whole of the alumina dissolves without carrying with it a trace of oxide of chromium.

(b.) *From the Alkaline Earths.*—This is also effected by fusing the mixture with carbonate of soda and nitre, the earths are thus obtained in the form of carbonates, and are separated from each other according to the instructions given (page 280).

(c.) *From the Alkalies.*—The oxide of chromium is precipitated by ammonia, sal-ammoniac having previously been added to the solution. The alkalies are determined in the filtrate according to the directions given (pp. 259 *et seq.*).

GROUP IV.

Zinc, Nickel, Cobalt, Manganese, Iron.

166. Zinc.

Oxide of Zinc is precipitated from its solutions, for the purpose of quantitative estimation, by a fixed alkaline carbonate, or by sulphide of ammonium; in either case it is subsequently brought to the state of oxide, in order to be weighed.

Precipitation as Basic Carbonate.—Carbonate of potassa or soda is added in excess to the solution, which is then boiled for some time; if, however, ammoniacal salts be present, a considerable excess of carbonate must be added, and the solution must be evaporated to dryness at the boiling temperature, in order to decompose the ammoniacal salts. The dry mass is well washed with hot water, and the residue, which is basic carbonate of zinc ($3HO,ZnO + 2ZnO,CO_2$), is strongly ignited, by which it becomes converted into oxide.

Precipitation as Sulphide.—The solution, if it be acid, is first supersaturated with ammonia, the alkali being added in sufficient quantity to redissolve the oxide of zinc, which first precipitates; sulphide of ammonium is then added till it no longer occasions a precipitate, and the sulphide of zinc, which is white, and very voluminous, is allowed completely to subside before

filtration; the sulphide is washed with water containing sulphide of ammonium, and then digested with concentrated hydrochloric acid until the solution ceases to smell of sulphuretted hydrogen; the resulting chloride of zinc is then precipitated as basic carbonate, and subsequently converted into oxide in the manner and with the precautions just described: it is to be observed, that it must not be neglected to examine whether the filtrate from the carbonate of zinc is free from *oxide of zinc*, which is done by adding to it a few drops of sulphide of ammonium; the formation of a white bulky precipitate indicates the presence of dissolved oxide of zinc, which must be collected and treated as above. The composition of *oxide of zinc* is—

One equivalent of Zn . .	32·75 . .	80·27
One ditto of O	8·00 . .	19·73
One ditto of ZnO . . .	40·75 . .	100·00

Separation of Oxide of Zinc from Oxide of Chromium, and from the Oxides of the Third, Second, and First Groups:—

(a.) *From Oxide of Chromium.*—The solution is mixed with tartaric acid, *excess* of potassa is then added, and the clear solution is precipitated with colourless sulphide of potassium; the sulphide of zinc is treated as above, the oxide of chromium is contained in the filtrate, and is obtained by evaporating it to dryness, and fusing the ignited residue with nitre and carbonate of soda, the alkaline chromate thus obtained is treated as directed (p. 293); when both the oxides are combined with acids that form soluble salts with baryta, their separation can, according to Fresenius, be accomplished by digesting the acid solution for several hours with excess of artificially prepared *carbonate of baryta:* the whole of the oxide of chromium is removed, and is mixed with the excess of carbonate of baryta, from which it is separated by dissolving in hydrochloric acid, and adding excess of sulphuric acid; the *oxide of zinc* remains in solution, and is precipitated by carbonate of potassa.

(b.) *From Alumina.*—The solution containing the two oxides is supersaturated with ammonia; alumina is precipitated, and oxide of zinc remains in solution. If, to a solution of the mixed oxides in sulphuric acid, excess of *cyanide of potassium* be added, heat being avoided, alumina is precipitated, and oxide of zinc retained in solution. If, to a solution of the two oxides in sulphuric acid, excess of *acetate of baryta* be added, and then sulphuretted hydrogen passed into the solution, sulphide of

zinc is precipitated, while alumina remains dissolved; the sulphide of zinc is separated from the sulphate of baryta by digesting the mixture in hydrochloric acid, the oxide of zinc is then precipitated from the solution as basic carbonate, and the alumina is precipitated by ammonia.

(c.) *From Magnesia.*—Chloride of ammonium is added to the solution, and then sufficient ammonia to retain both oxides in solution: the zinc is precipitated from the ammoniacal solution by sulphide of ammonium, and the magnesia in the filtrate determined in the usual manner. Another plan which has been proposed is to precipitate both oxides by carbonate of potassa; and then, having added a sufficient quantity of cyanide of potassium to dissolve the zinc, the whole is evaporated to dryness at a boiling temperature, a little more carbonate of potassa having first been added: on treating the dry mass with water, the magnesia remains undissolved, and the *zinco-cyanide of potassium* is held in solution.

(d.) *From the Alkalies and Alkaline Earths.*—The bases are all brought into the state of acetates by adding *acetate of baryta* to the sulphuric acid solution as above described: the zinc is precipitated by sulphide of ammonium. To separate *oxide of zinc* from *lime*, *baryta*, and *strontia*, it has been recommended to treat the mixed solution with carbonate of potassa, until it acquires an alkaline reaction, then to add excess of cyanide of potassium, and apply heat; the earthy carbonates remain undissolved, while that of zinc is taken up. The solution is boiled with hydrochloric and nitric acids, until all hydrocyanic acid is expelled, and the oxide of zinc is then precipitated with carbonate of soda, those precautions being taken which are necessary when a salt of ammonia is present.

Volumetric Determination of the amount of Zinc in ores and metallurgical products. (Max Schaffner.)

The principle of the method is as follows:—Oxide of zinc dissolves very readily in a mixture of ammonia and carbonate of ammonia; from this ammoniacal solution the zinc is completely precipitated by sulphide of sodium. Now if exactly as much sulphide of sodium is added as is necessary for the precipitation of the zinc, the amount of zinc may be calculated from that of the sulphide of sodium employed. It is impossible, however, to observe the moment exactly, when the necessary quantity of sulphide of sodium has been added, for which reason it is necessary to call in the aid of another reaction,

which shows the completion of the operation with certainty. This object is very simply and perfectly attained when a few drops of *perchloride of iron* are added to the ammoniacal solution, by which a voluminous red precipitate of hydrated oxide of iron is produced. If sulphide of sodium be then added, this red precipitate remains unchanged as long as the solution still contains zinc; but as soon as all the zinc is thrown down as hydrated sulphide of zinc the red suspended precipitate of hydrated oxide of iron becomes black, sulphide of iron being formed, and this is the sign that the operation is completed. The valuation of the sulphide of sodium is effected in the following way. About 0·2 grm. of chemically pure zinc are weighed and dissolved in hydrochloric acid, the ammoniacal fluid is then added, and afterwards the same number of drops of perchloride of iron which will be used in the analysis; sulphide of sodium is then poured in from the burette until the red precipitate appears black, the number of cubic centimètres employed is noted, the quantity serving for the blackening of the oxide of iron is deducted, and from this is calculated how much zinc is represented by 1 cubic centimètre of sulphide of sodium. The dilution of the sulphide of sodium is about right when 17 or 18 cub. cent. represent about 0·2 grm. of zinc. To determine the quantity of sulphide of sodium required to convert oxide of iron into sulphide, the following is the process adopted. Into a glass flask is put about as much water containing ammonia as there is fluid obtained in the analysis; to this is added the same number of drops of perchloride of iron as is employed in the analysis, and after this, the solution of sulphide of sodium, until the red colour of the precipitate has become converted into black. When well corked, the solution of sulphide of sodium remains for some time without alteration; it is however better to test it again when it has been standing for some days, especially as the new testing does not occupy more than 8 or 10 minutes. 1 gramme of substance is usually quite sufficient for investigation. With very poor substances, it is better to take 2 grammes; with very rich substances half a gramme is sufficient. In some rare cases nickel and cobalt are present in zinc ores, in which case caustic potassa is employed as a solvent instead of ammonia.

This method of assaying zinc ores is not given by the author as rigidly accurate, but he asserts that it is sufficiently so for practical purposes, provided care be taken that the ammoniacal

solution of the zinc is not too concentrated, in fact, if the solution be diluted, and that of the perchloride of iron be very concentrated, the separation is very complete and distinct.

167. Nickel.

Oxide of nickel is precipitated from its solutions either as *hydrated oxide*, by caustic potassa, or as *sulphide*, by sulphide of ammonium; in either case it is converted into anhydrous protoxide to be weighed.

Precipitation as Hydrated Protoxide.—Solution of pure caustic potassa is added, and the solution heated to boiling; the voluminous apple-green precipitate which is formed requires protracted washing with hot water, after which it is dried and ignited; ammoniacal salts do not interfere with the precipitation of oxide of nickel by caustic potassa, but with carbonate of potassa it is not so complete.

Precipitation by Sulphide of Ammonium.—The complete precipitation of nickel in the state of sulphide, by sulphide of ammonium is not easy, in consequence of the partial solubility of sulphide of nickel in that reagent. To ensure success the sulphide of ammonium must be perfectly saturated and colourless, and not added in great excess, the vessel must be covered, and placed in a warm situation; the fluid above the precipitate should be free from colour. The sulphide of nickel is washed on the filter with water to which a few drops of sulphide of ammonium have been added; it is then dried, transferred to a beaker, and digested at a gentle heat until completely dissolved, with concentrated aqua-regia; the filter is burnt, and the ashes added to the solution,—this is better than digesting the filter and precipitate together, since the presence of organic matter prevents the complete precipitation of oxide of nickel by caustic alkali. The solution, filtered from the precipitated sulphur, is precipitated by potassa, washed, dried, and ignited. The composition of anhydrous protoxide of nickel is—

One equivalent of Ni . .	29·5 . .	78·37
One ditto of O	8 . .	21·63
One ditto of Ni,O	37·5 . .	100·00

Separation of Oxide of Nickel from Oxides of Zinc and Chromium, and from the Oxides of the Third and Second Groups:—

(a.) *From Oxide of Zinc.*—Several methods have been proposed.

α. *Berzelius's method.* —The greater part of the oxide of zinc is first extracted by caustic potassa; the residue, after being well washed and heated, is mixed with pure *pulverized sugar*, and carefully carbonized in a porcelain crucible. The crucible is then surrounded with lime in a larger Hessian crucible, and heated for an hour in a blast-furnace as strongly as possible. The oxides are reduced, and the zinc is driven off in vapour; the nickel is dissolved in nitric acid, evaporated to dryness in a platinum crucible, and ignited. The loss of weight gives the quantity of oxide of zinc. The principal point to be attended to is to extract all the potassa from the mixed oxides: the sugar must be perfectly pure, with which view it should be crystallized from an alcoholic solution.

β. *Ullgren's method.*—The oxides are precipitated by carbonate of soda, the whole evaporated, and the residue gently heated, so that they remain perfectly insoluble when the mass is treated with water. The oxides are washed and dried, and then being placed in a tube with a bulb, are reduced by hydrogen at a low red-heat; the tube is allowed to cool, while a continuous current of hydrogen is passed through it; it is then closed at one end by fusion, filled with a concentrated solution of carbonate of ammonia, corked up, and placed in a warm situation for twenty-four hours; the *oxide of zinc*, which is not reduced, is dissolved in the carbonate of ammonia; the oxide of nickel *is* reduced, and the metal, after being well washed with carbonate of ammonia, is dried and weighed; the oxide of zinc is obtained from the ammoniacal solution by evaporation. The oxides must be finely pulverized before they are exposed to the action of hydrogen gas.

γ. *Rose's method.*—The mixed oxides, after having been ignited, are placed in the bulb of a reduction tube, which communicates on the one side with an apparatus, from which dry hydrochloric acid gas is liberated, and, on the other, with a flask containing a very dilute solution of ammonia. As soon as the air is expelled, the bulb is gradually heated to redness, the oxides are converted into chlorides, the chloride of nickel remains in the bulb, and the volatile chloride of zinc passes into the solution of ammonia, in which it dissolves. The oxides are then determined in the usual manner. This method, though tedious and somewhat complicated, yields very accurate results.

δ. *Smith's method.*—The oxides are converted into acetates; and, excess of acetic acid being added, sulphuretted hydrogen

is passed through the solution, by which the whole of the zinc is precipitated as sulphide, while the oxide of nickel remains in solution: this method, which is well adapted for the analysis of *German silver*, the constituents of which are *copper*, *zinc*, and *nickel*, has been found by M. Louyet to yield very accurate results.

ε. *Brunner's method.*—The solution of the two metals in hydrochloric or nitric acid is diluted with a large quantity of water, and almost completely neutralized with carbonate of soda. To effect this a slight excess of the latter is added, and the precipitate which ensues is redissolved in a few drops of acid, so as to introduce a very slight excess of the latter. A current of sulphuretted hydrogen is then made to pass through the liquid, and to complete the precipitation of the zinc, a few drops of a diluted solution of acetate of soda are added. Care must be taken not to introduce an excess of acetate, and not to heat the liquid. A fresh current of sulphuretted hydrogen is now allowed to pass, until the precipitate does not appear to increase. The vessel is then left to itself for ten or twelve hours, at the ordinary temperature, after which the precipitate is collected on a filter, and washed. To make sure that all the zinc has been thrown down, a drop of acetate of soda may be added to a little of the filtered liquid, which should remain clear, when a little sulphuretted hydrogen is introduced. The nickel is thrown down from the filtrate by potassa. If the original solution contain iron, it is essential to separate it first of all, by carbonate of baryta.

Field prefers *hypochlorite of soda* as a precipitant for nickel; the metal is thrown down as *peroxide*, which, after boiling the solution in which it is suspended, separates as a rather dense precipitate, which can be easily washed, whilst the bulky gelatinous *protoxide* thrown down by potassa is washed with difficulty, the alkali adhering with remarkable pertinacity to the hydrated oxide. The precipitation should be effected in a beaker. The peroxide is heated to whiteness, and the nickel weighed as protoxide.

(b.) *From Oxide of Chromium.*—The mixed oxides are fused with nitre and carbonate of soda; the oxide of chromium is thus converted into *chromic* acid, and is dissolved on boiling with water as alkaline chromate.

(c.) *From Alumina.*—Excess of cyanide of potassium is added, heat being avoided; alumina is precipitated, and oxide

of nickel retained in solution: according to Berthier, on adding *sulphite of ammonia* to a solution of the two oxides, the alumina only is precipitated.

(d.) *From Magnesia.*—This is effected in the same manner as the separation of oxide of zinc from the same earth.

(e.) *From Baryta, Strontia, and Lime.*—Cyanide of potassium is added in excess, and then carbonate of potassa, the whole is boiled, and the insoluble carbonates separated by filtration from the *nickel cyanide.* The solution is boiled with hydrochloric acid until all the hydrocyanic acid is expelled; potassa in excess is then added, and the solution boiled till all the ammonia is liberated; the oxide of nickel is then precipitated by potassa.

Lewis Thompson thinks that absolutely pure nickel has not hitherto been obtained in quantity. He prepared it by reducing granulated oxide of nickel by hydrogen gas in a red-hot porcelain tube. When fused, the button obtained was white and silvery-looking; its specific gravity was 8·575, and it was almost as soft as copper; it could be rolled out nearly to the thinness of tinfoil; its malleability was therefore very great. Thompson suggests, as a great improvement in the metallurgy of this metal, to reduce the common ore (the arsenio-sulphuret) after washing, by mixing it with half its weight of chalk, and strongly heating in a cubilo-furnace in full blast; the use of the large quantity of arsenic on which the present practice depends is thus avoided, and there is no appreciable loss of metal.

If we have in solution a mixture of sulphates of *nickel, cobalt, zinc, manganese, iron,* and *copper,* almost every particle of *nickel* and *cobalt* may, according to Thompson, be separated as a green crystalline powder by adding to the solution in a warm state as much sulphate of ammonia as it will dissolve; this separation depends on the fact that the sulphates of nickel and cobalt form with sulphate of ammonia *triple alums,* which are absolutely insoluble in cold saturated solutions of sulphate of ammonia.

Analysis of Kupfernickel (Ebelmen).—The purified mineral is treated with aqua-regia. The sulphuric acid is precipitated by chloride of barium, and the excess of barium being removed by sulphuric acid, the arsenic acid is converted into arsenious acid by ebullition with sulphurous acid, and then precipitated by sulphuretted hydrogen. The sulphide of arsenic obtained is after drying and weighing, decomposed by aqua-regia, to obtain

the sulphur. The liquor freed from sulphide of arsenic is concentrated with the addition of nitric acid, and precipitated by excess of ammonia; an abundant precipitate of peroxide of iron is formed, which generally retains a little nickel. It is redissolved on the filter by hydrochloric acid, and the liquor treated cold with carbonate of baryta. The peroxide of iron alone is precipitated; the carbonate of baryta with which it was mixed is readily separated. The liquor containing the nickel is treated with sulphuric acid, and after filtration is added to the ammoniacal solution of the rest of the nickel: this is precipitated by excess of potassa, and, after drying and calcining, is weighed; its quantity indicates that of the metallic nickel. The ammoniacal liquor, afterwards treated with hydrosulphate of ammonia, sometimes yields a black precipitate, which, collected, calcined, and weighed, gives with borax the reaction of cobalt. ('Annales des Mines,' tome xi. p. 56.)

168. Cobalt.

This metal is precipitated from its solutions either by caustic potassa or by sulphide of ammonium. It is weighed either as *oxide* or in the *metallic state;* when great or even moderate accuracy is required, it must be estimated in the latter form, as the ignited hydrated protoxide is of indefinite composition, varying according to the degree of heat employed.

Precipitation as Hydrated Protoxide.—The solution is boiled with excess of caustic potassa; the precipitate, which at first is bluish, becomes, after long boiling, of a dirty rose-red colour; if ammoniacal salts are present, they must be decomposed, and the ammonia discharged by long-continued boiling, with great excess of caustic alkali; the precipitated hydrate requires long-continued washing with hot water; on being dried and ignited it turns black: in this state it is weighed; if the operator has determined on reducing it to reguline cobalt, he proceeds in the following manner:—

Reduction of Oxide of Cobalt to Reguline Cobalt.—The small bulb-tube of hard glass attached to the U-shaped chloride of calcium tube *b*, Fig. 71, having been carefully weighed, a certain known quantity of the previously weighed oxide is introduced, and the weight of the bulb-tube again accurately noted; a stream of hydrogen gas, dried by passing through the U-shaped chloride of calcium tube *b*, is then caused to flow through the apparatus from the flask *a*, and a flame applied to the bulb containing the

oxide; the heat must at first be gentle, but it must gradually be raised to full redness, this high temperature being necessary to prevent the reduced metal from acquiring a pyrophoric property, which would cause it to inflame on coming in contact with atmospheric air; the hydrogen reduces the metallic oxide, giving rise to a proportional amount of water, which escapes

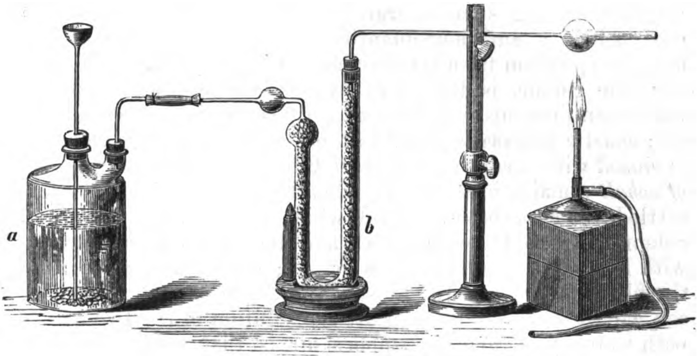


Fig. 71.

in the form of steam. When it is seen that water no longer continues to form, the flame is removed from the bulb, and it is allowed to cool, while a stream of hydrogen still continues to pass over it; the bulb-tube is then again weighed, and from the amount of reduced metal obtained the quantity contained in the whole of the protoxide precipitated, is calculated. If a sufficiently high temperature has not been employed, the reduced cobalt oxidizes at common temperatures, but if a full red-heat has been employed it absorbs oxygen very slowly.

Precipitation as Sulphide.—Sal-ammoniac is added to the solution, then slight excess of ammonia, and finally sulphide of ammonium as long as precipitation takes place; the resulting sulphide of cobalt is washed with water containing a little sulphide of ammonium, then digested with aqua-regia, and precipitated by potassa, precisely as sulphide of nickel. The hydrated oxide, after being washed, dried, and ignited, is reduced by hydrogen in the manner just described. Rose recommends that, in the presence of ammoniacal salts, cobalt should always be precipitated by sulphide of ammonium.

Separation of Oxide of Cobalt from Oxides of Nickel, Zinc,

and Chromium, and from the oxides of the third and second groups:—

(a.) *From Nickel.*—Several methods have been proposed by different chemists, but until recently Phillips's process was the one generally preferred, which is as follows:—

a. Method of Phillips.—Both oxides are dissolved in an acid, and the solution supersaturated with ammonia, having previously added a sufficient quantity of sal-ammoniac to prevent any precipitation from taking place; the solution, which has a sky-blue colour, is largely diluted with water, which should have been previously well boiled, to free it from atmospheric air: caustic potassa is added to the hot solution, and the vessel is closed with a cork; *oxide of nickel* is precipitated, and *oxide of cobalt* remains in solution; when the former has completely settled, the supernatant liquid, which should have a rose-red colour, is poured through a filter, and the oxide of nickel washed with hot water, ignited, and weighed; the oxide of cobalt in the filtrate is precipitated by sulphide of ammonium. The reason why it is necessary to dilute the solution of the two oxides with water, free from atmospheric air, is, that oxide of cobalt in an ammoniacal solution is converted into peroxide of cobalt, which, precipitating as a black powder, would contaminate the oxide of nickel. The more dilute the solution is, the less easily does the oxide of cobalt become oxidized. When a large quantity of ammoniacal salt is present, the quantity of caustic potassa required to precipitate the oxide of nickel is very considerable. According to Fresenius the separation by this method is not complete, the cobalt invariably containing traces of nickel, and the precipitated nickel often, traces of cobalt.

β. Liebig's method.—This is founded on the following considerations:—When any salt of cobalt is warmed with cyanide of potassium and an excess of hydrocyanic acid, it is converted into the *percyanide of cobalt* and *potassium*, or *cobalticyanide of potassium* (Co_2Cy_6,K_3), the aqueous solution of which does *not* undergo any decomposition by boiling with either of the mineral acids. On the other hand, the precipitate produced by cyanide of potassium in solutions of salts of nickel is redissolved by cyanide of potassium, but the solution *is* decomposed by dilute sulphuric acid, cyanide of nickel being precipitated. When, therefore, a mixture of a cobalt and a nickel salt containing free acid is treated with excess of cyanide of potassium, and slightly warmed, we obtain in solution the double cyanide

of nickel and potassium, and cobalticyanide of potassium, ($NiCy + KCy$) + ($Co_2Cy_6K_3$,) and, on adding dilute sulphuric acid in the cold, three cases present themselves.

I. If the cobalt and nickel exist in the solution in the proportion by weight of *two* cobalt to *three* nickel, we have in the solution, $3(NiCy, KCy) + (Co_2Cy_6K_3)$, and the three equivalents of nickel replacing the three equivalents of potassium in the cobalticyanide of potassium, produce cobalticyanide of nickel ($Co_2Cy_6Ni_3$), which is precipitated of a bluish-white colour, leaving in the solution no trace of either cobalt or nickel.

II. If the solution contain *less* nickel than corresponds to the above proportions, a certain quantity of cobalticyanide of potassium remains in solution, while cobalticyanide of nickel is still precipitated.

III. If the solution contain *more* nickel than corresponds to the above proportions, cobalticyanide of nickel is still precipitated, together with the excess of cyanide of nickel, which, by long boiling with hydrochloric acid, is completely converted into chloride of nickel, which remains in solution.

Now cobalticyanide of nickel, though insoluble in hydrochloric acid, is decomposed by boiling with caustic potassa into protoxide of nickel and cobalticyanide of potassium, thus, $Co_2Cy_6Ni_3 + 3KO = Co_2Cy_6K_3 + 3NiO$, and chloride of nickel is also decomposed by caustic potassa into protoxide of nickel and chloride of potassium. Hence, the following method of analysing mixtures of cobalt and nickel, which is applicable to all proportions.

Hydrochloric acid is added to the solution of the metals, and then cyanide of potassium in such excess that the precipitate at first formed is redissolved; the whole is boiled, adding from time to time hydrochloric acid, until hydrocyanic acid ceases to be evolved. Caustic potassa is then added in considerable excess, and the boiling continued until the hydrated protoxide of nickel is completely precipitated; it is then filtered, the filtrate contains the whole of the cobalt in the form of cobalticyanide of potassium; it is evaporated to dryness with excess of nitric acid, the residue fused, and treated with hot water: peroxide of cobalt remains, which is dissolved in hydrochloric acid, and the solution treated as already directed.

When a mixture of the two oxides is dissolved in hydrocyanic acid and potassa, and the solution kept boiling in a flask,

the cobalt becomes converted into cobalticyanide of potassium, and the nickel into protocyanide of nickel and potassium; all the cyanogen is extracted from the latter by *oxide of mercury*, by which the nickel is precipitated in the form of oxide; oxide of mercury produces no change in the cobalt compound. Instead of adding oxide of mercury to the cold solution of the mixed cyanides, this may be supersaturated with chlorine, and the resulting protocyanide of nickel again dissolved by caustic potassa. The chlorine has no action on the cobalt compound, whilst the nickel compound is decomposed, and all the nickel is at last precipitated as black peroxide. The operation must not be performed with heat, as otherwise Co_2O_3 is precipitated with the nickel, and care must be taken that during the introduction of the chlorine the fluid is kept strongly alkaline.

In analysing ores of nickel, which contain small quantities only of cobalt, considerable excess of hydrochloric acid must be taken to precipitate the cyanides dissolved in cyanide of potassium, and the mixture must be continued in ebullition for a full hour.

γ. *Rose's method.*—This is founded on the greater tendency in the protoxide of cobalt than in the protoxide of nickel to pass to a higher degree of oxidation. Both metals are dissolved in hydrochloric acid; the solution must contain a sufficient excess of free acid: it is then diluted with much water; if 20 or 30 grains of the oxides are operated on, about 2 pints of water are added to the solution. As cobalt possesses a much higher colouring power than nickel, not only in fluxes but also in solutions, the diluted solution is of a rose colour, even when the quantity of nickel present greatly exceeds that of the cobalt. A current of chlorine is then passed through the solution for several hours;* the fluid must be thoroughly saturated with it, and the upper part of the flask above the liquid must remain filled with the gas after the current has ceased. Carbonate of baryta in excess is then added, and the whole allowed to stand for 12 or 18 hours, and frequently agitated; the precipitated peroxide of cobalt, and the excess of carbonate of baryta, are well washed with cold water, and dissolved in hot hydrochloric acid; after the separation of the baryta by sulphuric acid, the cobalt is precipitated by hydrate of potassa, and, after being

* Mr. Henry recommends a solution of *bromine*, which is to be added till the solution smells strongly of it; he found this to answer equally well with chlorine, and the process is rendered less tedious and unpleasant.

washed and dried, is reduced by hydrogen gas, in the manner shown in Fig. 71. The fluid filtered from the oxide of cobalt is of a pure green colour; it is free from any trace of cobalt. After the removal of the baryta by means of sulphuric acid, the oxide of nickel is precipitated by caustic potassa. To ensure accurate results, it is indispensably necessary to wait a considerable time, at least 12, or even better 18 hours after the addition of the carbonate of baryta, as the oxide of cobalt is precipitated very slowly.

δ. *Another method.*—The two oxides are covered with hydrocyanic acid, and then potassa added till a portion remains undissolved. The solution is kept boiling for a quarter of an hour, moist hydrated oxide of mercury is then added till a portion remains undissolved; a green precipitate occurs containing all the nickel, with the excess of oxide of mercury. By ignition, pure oxide of nickel remains. Acetic acid is added to the filtrate to aid reaction; it is then precipitated with blue vitriol. The blue precipitate contains all the cobalt; this is dried, ignited, redissolved in hydrochloric acid, the copper, precipitated by sulphuretted hydrogen, and then from the filtrate, the cobalt by potassa. The method depends upon the fact, that *nickelo*-cyanide of potassium is decomposed by oxide of mercury, while *cobalto*-cyanide of potassium experiences no change.

(b.) *From Oxide of Zinc.*—The above method may, according to Rose, be employed for the separation of these two oxides; and also for that of other oxides from oxide of cobalt, which are strongly basic, and which are not converted into superoxides: oxide of zinc may likewise be separated from oxide of cobalt by Liebig's process with cyanide of potassium, cobalticyanide of zinc is gradually dissolved in boiling hydrochloric acid, and a clear solution is obtained: on the addition of caustic potassa and boiling, both the cobalt and the zinc are retained in solution, the former as cobalticyanide of potassium, and the latter as oxide, and from the solution, zinc is precipitated, by sulphuretted hydrogen (Brunner): the methods of Berzelius, Ullgren, and for the separation of oxide of nickel from oxide of zinc may likewise be employed for the separation of oxide of cobalt.

(c.) *From Oxide of Chromium.*—This is effected in the same manner as the separation of oxide of nickel from oxide of chromium.

(d.) *From Alumina.*—Cyanide of potassium is added, heat being avoided; the cobalt is dissolved as cobalticyanide of

potassium, and the alumina precipitated; according to Berthier, the separation may likewise be effected by sulphite of ammonia.

(e.) *From the Alkaline Earths.*—This is effected in the same manner as the separation of the oxide of nickel.

Analysis of Cobalt Ores, containing Cobalt, Nickel, and Iron. (Liebig.)—Add to the hot acid solution ammonia till slightly alkaline, then succinate or benzoate of ammonia to throw down the iron. Precipitate the filtrate by potassa, and filter. Wash the oxides of *cobalt* and *nickel* repeatedly; dissolve them in pure cyanide of potassium, then boil with an excess of fresh precipitated oxide of mercury. The whole of the nickel deposits with the excess of oxide of mercury. Filter, saturate with acetic acid: boil; then add sulphate of copper, and reboil. The precipitate has the following formula: $Cu_3Co_2Cy_6$. Collect it, and ignite, to destroy the cyanogen; dissolve in aqua-regia, and separate the copper by sulphuretted hydrogen; this precipitate must be redissolved, and the oxide of copper precipitated by potassa. From the amount of copper that of cobalt is calculated. Three equivalents of copper are equal to two of cobalt.

Extraction of Cobalt and Nickel from the Ore.—The following process is followed in a manufactory at Birmingham, the ore employed consisting principally of metallic sulpho-arseniurets, and containing generally about 6 per cent. of nickel and 3 per cent. of cobalt. The ore is mixed with a small quantity of carbonate of lime and fluor-spar, and the whole is heated to a white-red heat in a reverberatory furnace: the mass fuses at this high temperature, and a slag is obtained floating on the surface of a fluid mass, of metallic appearance; the latter is let out of the furnace by a particular aperture, and watered in order that it may be broken into fragments with greater facility. It has been ascertained from experience that when the slag is of a dull colour, iron is present, but if its surface be black and brilliant, it is free from that metal. The metallic mass is reduced to a very fine powder, which is calcined at a bright-red heat in a furnace, the temperature being graduated so as to avoid fusion, and constantly raked: a considerable quantity of arsenious acid is driven off. The air has free access to the mass, which becomes oxidized and diminished in weight. The calcination, which lasts for about twelve hours, is continued until no more white fumes are given off, and the

residue is treated with hydrochloric acid, which dissolves nearly the whole of it: the liquid is diluted with water, and milk of lime and chloride of lime added to precipitate the iron and the arsenic; the precipitate, after being well washed, is thrown away. A current of washed sulphuretted hydrogen, generated from sulphide of iron and dilute sulphuric acid, is passed into the liquor until it is saturated: it is discontinued, when some ammonia, added to a sample of the filtered liquor, gives a black precipitate; if there was not an excess of sulphuretted hydrogen, the precipitate produced by ammonia would be green: the precipitate is washed and then thrown away, a current of sulphuretted hydrogen being passed into the wash waters. The cobalt is then thrown down with a solution of hypochlorite of lime. The precipitate, washed, dried, and then heated to redness, is considered to be oxide of cobalt, and part is sent in this state into the market. Another portion is heated to a white-red; by this treatment the oxide loses in weight, but increases in density; it is sold as protoxide of cobalt. The liquid from which the cobalt has been precipitated is treated with milk of lime, which precipitates the nickel in the state of hydrate: this precipitate is washed, dried, and heated to redness; it is then mixed with charcoal, and, by means of a strong heat, reduced to the state of a spongy nickel, which is employed in the manufacture of German silver. The oxide of cobalt thus prepared is remarkably pure.

169. Iron.

This metal is weighed as sesquioxide; if it exist in the solution in the form of a *protosalt*, it must be peroxidized by heating with nitric acid as long as fumes of nitrous vapour are discharged, or by boiling with chlorate of potassa and hydrochloric acid: ammonia is the precipitant employed, as the oxide precipitated by potassa or soda is always contaminated by a certain quantity of the alkali, from which it is almost impossible to free it by washing: the hydrated sesquioxide shrinks greatly on drying, and, by ignition, loses all its water. Iron is sometimes precipitated as sulphide by sulphide of ammonium: the solution must not contain free acid: it must be well washed on the filter with water, to which a few drops of sulphide of ammonium have been added, the funnel being protected from the air with a glass plate to prevent a portion of the sulphide from becoming oxidized into sulphate, which

would dissolve and be carried through the filter: the washed sulphide is, together with the filter, digested with dilute hydrochloric acid, filtered, and the filtrate peroxidized by nitric acid and precipitated by ammonia. When iron has to be separated from other bases, it is sometimes precipitated by ***succinate of ammonia:*** the solution must be very exactly neutralized by ammonia, the alkali being added in drops in a very diluted state until the small quantity of sesquioxide of iron which it precipitates is not redissolved by applying a gentle heat, the supernatant liquid possessing a red colour; the neutral succinate of ammonia is then added, upon which succinate of peroxide of iron of a brown colour is precipitated; it is filtered when quite cold, and washed first with cold water, and, finally, with a warm solution of ammonia, in order to remove a portion of the succinic acid: it is then dried, and ignited in a current of air, in order thoroughly to peroxidize the iron. The composition of sesquioxide of iron is—

Two equivalents	of Fe	.. 56	.. 70
Three ditto	of O	.. 24	.. 30
One ditto	of Fe_2O_3	80	100

Separation of Peroxide of Iron from Protoxide of Iron.— This is attended with difficulty, and can only be accomplished when the compound is soluble in acids. When no other base but iron is present, as, for example, in native magnetic iron ore, Rose directs that a weighed quantity of the substance should be dissolved in hydrochloric acid, and having boiled with nitric acid to peroxidize the whole of the iron, it is to be precipitated by ammonia; the increase of weight is owing to the acquisition of oxygen, which has combined with the protoxide of the compound, and is ***half as much in quantity*** as the oxygen previously existing in the protoxide, for the protoxide of iron, on being fully converted into peroxide, acquires one-half more oxygen than it already possessed.

$$2(FeO)+O=Fe_2O_3$$

Thus then, finding first the quantity of oxygen gained by the substance operated on, we find next the quantity of oxygen belonging to the protoxide existing in the compound, and from this it is easy to calculate the quantity of the protoxide. When this is found, the quantity of peroxide contained in the substance is learned from the difference in weight between

the quantity of the compound submitted to analysis and the quantity of protoxide made out by calculation. It is easy, however, to see that as the proportion of protoxide of iron is generally small in comparison with that of peroxide, the greatest accuracy in experimenting is necessary, in order to arrive at correct results, a very trifling error becoming a very considerable one in the subsequent calculation of the quantity of protoxide.

Another method, given by Rose, for determining the quantity of oxygen in a compound consisting merely of protoxide and peroxide of iron, is by converting the oxides into metallic iron by igniting them in a current of dry hydrogen gas, and determining not only the quantity of iron revived, but also the weight of the water formed.

To determine experimentally the quantity of peroxide of iron in a soluble compound of peroxide and protoxide, a weighed quantity of the pulverized mixture is introduced into a flask, the whole of the atmospheric air from which is then expelled by a current of carbonic acid gas; hydrochloric acid sufficient to dissolve the compound is then added, and the flask quickly and securely closed. Solution being effected, recently prepared perfectly clear sulphuretted hydrogen water is added in excess, and the flask again closed, and allowed to remain at rest for some days; the peroxide of iron is reduced to protoxide by the sulphuretted hydrogen, and a proportional quantity of sulphur is deposited; this is carefully collected on a small weighed filter, washed and dried at a gentle heat; the filter must be protected from the atmosphere during the process of filtration; from the weight of the sulphur the quantity of oxygen that has entered into combination with the hydrogen of the decomposed sulphuretted hydrogen is found; this oxygen was derived from the peroxide of iron; and, by multiplying it by three, the whole quantity of oxygen that was present in the substance in the form of sesquioxide of iron is found.

Another method (Fresenius).—A known quantity of the finely divided substance is introduced into the flask A (Fig. 72), which is then filled with carbonic acid through the tube *d*; hydrochloric acid, not in great excess, is then added through the funnel *c*, and the solution of the compound assisted by heat, a steam of carbonic acid passing all the time through the apparatus; hot water is next added, and the solution

boiled and allowed to cool; pure recently precipitated carbonate of baryta is now mixed into a milky fluid, and poured into the flask through the funnel till it predominates; the whole mixture is then digested at a very gentle heat. The flask is filled with boiling water nearly up to the end of the tube *b*, which, being depressed as far as necessary into the liquid, the clear fluid is drawn off; the tube is then raised, and the flask again filled with water; when the precipitate has settled, the clear fluid is again drawn off by the siphon *b*, the flask is then rinsed out with boiling water, and the precipitate thrown on a filter, and well washed with boiling water, as much as possible out of access of air: the amount of peroxide of iron in the washed precipitate is then determined. The liquid is drawn off by the siphon, and the filtrate from the precipitate contains the whole of the dissolved protoxide of iron; the solution is concentrated, the iron peroxidized, and, finally, precipitated, after the removal of the *baryta*.

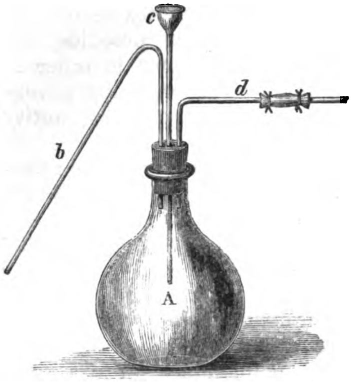


Fig. 72.

Indirect method (Rose).—A weighed portion of the substance is dissolved in hydrochloric acid in a flask, which has previously been filled with carbonic acid gas; the solution being effected, solution of *chloride of gold* and *sodium* is added in excess, and the flask closed; reduction takes place, and metallic gold is precipitated, which is collected, washed, ignited, and weighed; from the quantity obtained, the quantity of oxygen, which was necessary to convert the protoxide of iron into peroxide, is ascertained by calculation, thus—

$$6FeCl + AuCl_3 = 3Fe_2Cl_3 + Au.$$

One equivalent of precipitated gold corresponds to six equivalents of protochloride or protoxide of iron.

Another method (Fuch).—A weighed portion of the substance is dissolved, as in Rose's method, in hydrochloric acid, in a flask which has previously been filled with carbonic acid gas;

a weighed slip of clean copper is introduced, and the flask, having been filled nearly to the brim with boiled water, accurately closed; the mixture is digested until the fluid becomes colourless, or nearly so; the slip of copper is then removed from the flask, dried, and weighed; the diminution in weight indicates the amount of chlorine consumed to convert the original protochloride of iron into perchloride, every equivalent of copper corresponding to an equivalent of chlorine, and every one equivalent of chlorine converting *two* equivalents of protochloride of iron into perchloride, $2FeCl + Cl = Fe_2Cl_3$; it follows that every equivalent of dissolved copper corresponds to two equivalents of perchloride of iron in the solution, or, what amounts to the same, to two equivalents of peroxide of iron present in the analysed substance. The quantity of iron actually present in the specimen must be determined by peroxidizing a solution of a weighed quantity, and precipitating by ammonia. The method is founded on the fact that when air is excluded, hydrochloric acid is incapable of dissolving copper; but that on the addition of peroxide of iron, or when that substance is already present in the mixture, the acid dissolves a quantity of copper corresponding thereto.

Separation of Oxide of Iron from Oxides of Nickel, Cobalt, Manganese, Zinc, and from the Oxides of the Third and Second Groups.

(a.) *From the Oxides of Nickel and Cobalt* (Field's method).—The solution containing the oxides in the form of nitrates is evaporated to dryness, and after the addition of water, litharge is added, and the whole boiled for ten minutes or a quarter of an hour. The iron is entirely precipitated, the nitrates of nickel, cobalt, and lead remaining in solution. After filtration, which can be effected with great readiness, dilute sulphuric acid is added, and on standing for sixteen hours, the sulphate of lead is filtered off, and the nickel and cobalt precipitated and estimated. The filter containing the peroxide of iron and excess of litharge is digested in dilute sulphuric acid, filtered and washed; the sesquioxide of iron in the filtrate is precipitated by ammonia.

(b.) *From Manganese.*—The iron in the solution is first brought to the state of sesquioxide, and is then precipitated by succinate or benzoate of ammonia, a sufficient quantity of sal-ammoniac having previously been added; the precipitated succinate is treated in the manner already described, and the

manganese in the filtrate is precipitated by carbonate of soda. Another method of separation is by digesting the solution of the two metals with excess of recently precipitated carbonate of baryta, which throws down the iron as basic carbonate of peroxide; the washed precipitate is dissolved in hydrochloric acid, the baryta separated by sulphuric acid, and the iron precipitated by ammonia; the filtrate from the basic carbonate of peroxide of iron contains the manganese, together with a soluble baryta salt, the latter is removed by sulphuric acid, and the manganese precipitated by carbonate of soda.

Another method (Field).—The solution containing the oxides is boiled with oxide of lead, by which the whole of the iron is precipitated; from the filtrate, the oxide of lead is precipitated by dilute sulphuric acid, and the sulphate of lead being filtered off, the oxide of manganese is precipitated from the filtrate by potassa. The mixed oxides of lead and iron are redissolved in dilute nitric acid, and then digested with dilute sulphuric acid, filtered and washed, and the sesquioxide in the filtrate precipitated by ammonia.

(c.) *From Zinc.*—The iron in the solution is peroxidized by nitric acid or by chlorate of potassa, the solution is evaporated to dryness, and all excess of acid removed; the residue is dissolved in acetic acid, and the zinc precipitated by sulphuretted hydrogen: the precipitated sulphide of zinc should have a pure white colour.

(d.) *From Chromium* (Rose).—To the solution of the two metals a sufficient quantity of tartaric acid is added to prevent the precipitation of either of the metals by potassa, that alkali is then added, and the iron precipitated by sulphide of potassium; the solution filtered from the sulphide of iron contains the oxide of chromium; it is evaporated to dryness, ignited, fused with carbonate of soda and nitre, and the chromium in the alkaline chromate thus formed determined as directed (page 290).

Another method (Berthier).—The oxides are precipitated by ammonia or carbonate of ammonia, and, while still moist, digested with slight excess of sulphurous acid: the whole of the iron dissolves, and also a certain quantity of the oxide of chromium, while the remainder of this latter metal is converted into pure subsulphite. The solution is boiled until it is decolorized, when it only contains iron. To precipitate this metal the sulphurous acid is either expelled by sulphuric acid,

or oxidized by aqua-regia, an alkali or an alkaline carbonate is then added; or the iron is precipitated by an alkaline sulphide without expelling the sulphurous acid.

Another method (Liebig).—The mixture of the two metals in solution is first saturated with sulphuretted hydrogen, to be certain that the iron is contained in the liquid as protoxide, (an addition of a few drops of sulphide of ammonium answers the purpose), and then thrown down by cyanide of potassium, and an excess of the latter added: the iron dissolves immediately as ferrocyanide of potassium, while the oxide of chromium remains behind.

(e.) *From Yttria* (Scherer).—To a neutral solution, oxalate of potassa is added, a white crystalline precipitate consisting of the double oxalate of yttria and potassa, is gradually formed, which, by ignition, is converted into yttria and carbonate of potassa; the mixture is dissolved in hydrochloric acid, diluted with much water, and the yttria precipitated by caustic ammonia, it must be well washed with boiling water, after which it may be ignited and weighed.

Another method (Berthier).—The moist hydrates are boiled with sulphurous acid, the yttria is deposited, and the iron remains in solution; to prevent the formation of an ochreous deposit from the action of the air, the solution should be boiled in a flask with a long neck, and when no more sulphurous acid is disengaged, it should be filled with boiling water and corked; when it has become cold, the liquid is decanted on to a filter replaced by boiling water, and finally filtered and edulcorated.

(f.) *From Alumina* (Weeren).—To the solution, containing the two oxides a sufficient quantity of tartaric acid is added to prevent the precipitation of the bases by ammonia, sulphide of ammonium is then added in excess, and the beaker covered with a glass plate till the whole of the sulphide of iron has precipitated. The clear supernatant liquid is then poured off, the precipitate thrown on a filter, and rapidly washed with water containing a little sulphide of ammonium. The sulphide of iron is dissolved off the filter by hydrochloric acid, and the iron having been peroxidized by nitric acid is precipitated by ammonia. The solution containing the whole of the alumina is evaporated to dryness and ignited strongly; if the amount of charcoal be small, it is to be completely burnt; but if it be considerable, it must be treated with boiling hydrochloric acid, and

the alumina precipitated from the filtered solution by sulphide of ammonium.

When a very small quantity of alumina is present, Reynolds recommends the addition to the solution of sufficient oxalic acid to prevent the precipitation of the earth, the solution is then poured into a mixture of ammonia and sulphide of ammonium, the precipitated sulphide of iron is treated as above, the solution containing the alumina is concentrated and then boiled with hydrochloric acid and chlorate of potassa, this will oxidize the oxalic acid and the sulphide of ammonium; the solution is now rendered alkaline with carbonate of ammonia, and boiled for some time, when the alumina will be precipitated.

When alumina has to be separated from oxide of iron, which is accompanied by manganese, lime, and magnesia, Richter fuses the compound with ten times its weight of carbonate of soda, and then, by means of water, with the addition of potassa, dissolves the alumina as aluminate of potassa and soda.

Another method (Fresenius).—The iron in the solution is reduced to the minimum of oxidation by boiling with sulphite of soda; it is then neutralized with carbonate of soda, an excess of caustic soda added, and the solution, after being well agitated, is boiled until it has become black and granular (a coil of platinum wire put into the flask prevents succussion); it is allowed to subside, the clear liquid passed through a close filter, and the precipitate washed with hot water, at first by decantation and then on the filter; the filtered solution treated with hydrochloric acid and chlorate of potassa furnishes, upon precipitation with ammonia, and several hours' standing, the whole of the alumina in a perfectly pure state.

(g.) *From Lime and Magnesia* (Rose).—Ammonia is added in excess, and the liquid boiled; a little lime is carried down in the precipitate, but it is completely redissolved on ebullition; the lime in the filtrate is precipitated by oxalic acid, and the magnesia in the state of ammonio-phosphate of magnesia: or the hydrochloric solution of the oxides may be diluted and neutralized as far as practicable with ammonia, and the oxide of iron then precipitated by succinate or benzoate of ammonia.

Dry assay of Iron ores.—The object of the dry assay of an iron ore is to ascertain, by an experiment on a small scale, the amount of iron which the ore should yield when smelted on the large scale in the blast furnace. For this purpose the

metal must be deoxidized, and such a temperature produced as to melt the metal and the earths associated with it in the ore, so that the former may be obtained as a dense button at the bottom of the crucible, and the latter in a lighter glass or slag above it. Such a temperature can only be obtained in a wind furnace, connected with a chimney at least thirty feet high; and when made expressly for assaying, the furnace is generally built of such a size that four assays may be made at the same time, namely about fourteen inches square and two feet in depth from the under side of the cover to the moveable bars of iron which form the grate. In order that the substances associated with the iron in the ore, should form a fusible compound it is usually requisite to add a flux, the nature of which will depend on the character of the ore under examination. Berthier divides iron ores into five classes:—1. The almost pure oxides, such as the *magnetic oxide*, *ologistic iron*, and the *hæmatites*. 2. Ores containing silica, but free, or nearly so, from any other admixture. 3. Ores containing silica and various bases, such as *lime*, *magnesia*, *alumina*, *oxide of manganese*, *oxide of titanium*, *oxide of tantalum*, *oxide of chromium*, or *oxide of tungsten*, but little or no *silica*. 5. Ores containing *silica*, *lime*, and *another base*, and which are fusible alone. Ores of the first class may be reduced without any flux; but it is always better to employ one, as it greatly facilitates the formation of the button: borax may be used, or better, a fusible earthy silicate, such as ordinary flint-glass. Ores of the second class require some base to serve as a flux, such as carbonate of soda, or a mixture of carbonate of lime and clay, or of carbonate of lime and dolomite. Ores of the third class are mixed with carbonate of lime in the proportion of from one-half to three-fourths of the weight of the foreign matter present in the ore. Ores of the fourth class require as a flux silica in the form of rounded quartz, and generally also some lime. The manganesian spathic ores which belong to this class, may be assayed with the addition of silica alone, but the magnesian spathic ores require lime. Ores of the fifth class require no flux.

Method of conducting the assay.—One hundred grains of the ore finely pulverized, and passed through a silk sieve, are well mixed with the flux, and the mixture introduced into the smooth concavity made in the centre of a crucible that has been lined with charcoal. The lining of the crucible is effected

by partially filling it with coarsely powdered and slightly damped charcoal, which is then rammed into a solid form by the use of a light wooden pestle. The mingled ore and flux must be covered with charcoal. The crucible thus filled, is closed with an earthen lid luted on with fire clay, and is then set on its base in the air-furnace. The heat should be very slowly raised; the damper remaining closed during the first half-hour. In this way the water of the damp charcoal exhales slowly, and the deoxidation of the ore is completed before the fusion begins; if the heat were too high at first, the luting would probably split, and moreover the slag formed would dissolve some oxide of iron, which would of course be lost to the button, and thus give an erroneous result. After half an hour the damper is gradually opened, and the furnace being filled with fresh coke, the temperature is raised progressively to a white heat, at which pitch it must be maintained for a quarter of an hour: the damper is then closed, and the furnace allowed to cool. As soon as the temperature is sufficiently reduced, the crucible is removed, and opened over a sheet of brown paper; the *brasque* is carefully removed, and the button of cast iron taken out and weighed. If the experiment has been entirely successful, the iron will be found at the bottom of the crucible in a small rounded button, and the slag will be entirely free from any adhering metallic globules, and will resemble in appearance green bottle-glass; should, however, the slag contain small metallic particles, the experiment is not necessarily a failure, as they may generally be recovered by washing, and the magnet: but if, on breaking the crucible, the reduced metal should be found in a partially melted state, and not collected into a distinct mass, it indicates either too low a temperature or an improper selection of fluxes, and the experiment must be repeated. The iron obtained is not chemically pure; it contains *carbon*, and, if the ore be manganiferous, *manganese:* the result is therefore somewhat too high, though indicating with sufficient exactness for all manufacturing purposes, the richness of the ore assayed.

Humid assay of iron ores.—Too great care cannot be bestowed on the *sampling* of ores intended for analysis. To expend so much time and labour on an isolated specimen (unless for a special object) is worse than useless. The sample operated upon should be selected from a large heap which should be thoroughly gone over, and several pieces taken from

different parts; these should be coarsely powdered and mixed, and about half a pound taken from the mass should be preserved in a well-stoppered bottle for the analysis.

(1.) *Determination of water (hygroscopic and combined).*—About 50 grains of the ore are dried in the water-oven, Fig. 61 B, till no further loss of weight takes place; the loss indicates hygroscopic water; the residue is introduced into a tube of hard glass, to which is adapted a weighed tube containing chloride of calcium; the powder is then gradually raised to a low red-heat, the combined water is thereby expelled, and its amount determined by the increase in weight of the chloride of calcium tube. Some ores (the hydrated hæmatites) contain as much as 12 per cent. of combined water.

(2.) *Sulphuric acid and sulphur.*—From 30 to 50 grains of the ore are digested with hydrochloric acid, filtered and washed. The filtrate, concentrated, if necessary, by evaporation, is precipitated by excess of chloride of barium. The insoluble residue on the filter is fused in a platinum or gold crucible, with nitre and carbonate of soda; the fused mass is dissolved in hydrochloric acid, evaporated to dryness, redissolved in dilute hydrochloric acid, filtered, and precipitated as before, by chloride of barium; even 100 parts of the sulphate of baryta produced indicate 13·734 parts of sulphur, corresponding with 25·48 parts of pyrites. In the analysis of hæmatites it is necessary to bear in mind that perchloride of iron is partially reduced when boiled with finely divided iron pyrites and hydrochloric acid, sulphuric acid being formed. (Dick.)

(3.) *Phosphoric acid.*—From 50 to 75 grains of the ore are digested with hydrochloric acid and filtered. The clear solution, which should not be too acid, is boiled with sulphite of ammonia, added gradually in small quantities, till it either becomes colourless or acquires a pale green colour, indicating that the peroxide of iron originally present has been reduced to protoxide. The solution is nearly neutralized with carbonate of ammonia, excess of acetate of ammonia added, and the liquid boiled; strong solution of perchloride of iron is then added, drop by drop, until the precipitate which forms has a distinct red colour: this precipitate, which contains all the phosphoric acid originally present in the ore, is collected on a filter, washed, and redissolved in hydrochloric acid, tartaric acid added, and then ammonia. From this ammoniacal solution the phosphoric acid is finally precipitated as ammonio-

magnesian phosphate, by the addition of chloride of ammonium, sulphate of magnesia, and ammonia. The precipitate is allowed 24 hours to subside, it is then collected on a filter, and if it has a yellow colour, which is almost invariably the case, it is redissolved in hydrochloric acid, and more tartaric acid being added, it is again precipitated by ammonia: 100 parts of the ignited pyrophosphate of magnesia correspond to 63·8 parts of phosphoric acid.

(4.) *Determination of the remaining constituents.*—25 or 30 grains of the finely-powdered ore are digested for about half an hour with strong hydrochloric acid, diluted with boiling distilled water, and filtered. The residue on the filter being thoroughly washed, the solution is peroxidized, if necessary, by the addition of chlorate of potassa, nearly neutralized by ammonia, boiled with excess of acetate of ammonia, and rapidly filtered while hot; the filtrate (which should be colourless) together with the washings, is received in a flask, ammonia is added, and then a few drops of bromine, and the flask closed with a cork. In a few minutes, if manganese be present, the liquid acquires a dark colour; it is allowed to remain at rest for 24 hours, then warmed, and rapidly filtered and washed; the brown substance on the filter is hydrated oxide of manganese: it loses its water by ignition, and then becomes Mn_3O_4, 100 parts of which correspond to 92·14 parts of protoxide.

The liquid filtered from the manganese contains the *lime* and *magnesia;* the former is precipitated by oxalate of ammonia, and the oxalate of lime formed converted by ignition into carbonate, in which state it is either weighed, having been previously evaporated with carbonate of ammonia, or it is converted into sulphate by the addition of a few drops of sulphuric acid, evaporation, and ignition. The lime being separated, the magnesia is thrown down as ammonio-magnesian phosphate by phosphate of soda and ammonia, and after standing for twenty-four hours it is collected on a filter, washed with cold ammonia-water, dried, ignited, and weighed; 100 parts of carbonate of lime correspond to 56·0 of lime; 100 parts of sulphate of lime to 40·1 of lime, and 100 parts of pyrophosphate of magnesia to 36·22 of magnesia.

The red precipitate collected on the filter after the boiling with acetate of ammonia, consists of the basic acetate of *iron,* and perhaps of alumina, together with the *phosphoric acid.* It is dissolved in a small quantity of hydrochloric acid, and then

boiled in a silver or platinum basin with considerable excess of pure caustic potassa; the alumina (with the phosphoric acid) is hereby dissolved, the insoluble portion is allowed to subside, and the clear liquid is then decanted, after which the residue is thrown on a filter and washed; the filtrate and washings are supersaturated with hydrochloric acid, nearly neutralized with ammonia, and the alumina finally precipitated by carbonate of ammonia. From the weight of the ignited precipitate, the corresponding amount of phosphoric acid determined by a separate operation is to be deducted, the remainder is calculated as *alumina*. The residue left after digesting the ore with hydrochloric acid, consists principally of *silica*, but it may also contain *alumina*, *peroxide of iron*, *lime*, *magnesia*, and *potassa*. For practical purposes it is rarely necessary to submit it to minute examination; should such be desired, it must be dried, ignited, and weighed, then fused in a platinum crucible with four times its weight of mixed alkaline carbonates, the fused mass dissolved in dilute hydrochloric acid, and evaporated to dryness, the residue moistened with strong hydrochloric acid, and after standing at rest for some hours, digested with hot water, filtered, and the *silica* on the filter ignited and weighed. The *alumina*, *lime*, *oxide of iron*, and *magnesia* in the filtrate are separated from each other according to the instructions given above; the *potassa* is estimated by a distinct process.

(5.) *Carbonic acid.*—This acid, which constitutes a considerable part of the weight of that large and important class of ores, the *clay ironstones*, is estimated by noting the loss sustained after adding to a weighed portion of the ore sulphuric acid, and thus evolving the gas (see "Carbonic Acid"); or more roughly, by the loss sustained in the entire analysis. Another method is to fuse 20 or 25 grains of the ore with 60 or 80 grains of dry borax, and noting the loss, which consists of water and carbonic acid; by deducting the water obtained in a previous experiment, the quantity of carbonic acid is obtained. This method, however, can scarcely be recommended on account of the corrosion of the crucible, though the results are very accurate.

(6.) *Determination of the iron.*—This is performed on a separate portion of the ore, either by the volumetric method of Marguerite, or by that of Dr. Penny: both give very exact results.

(a.) *Marguerite's method.*—This is based on the reciprocal action of the salts of protoxide of iron and permanganate of po-

tassa, whereby a quantity of the latter is decomposed exactly proportionate to the quantity of iron. The ore (about 10 or 15 grains) is dissolved in hydrochloric acid, and the metal brought to the minimum of oxidation by boiling the solution with *sulphite of soda* (or better, by pure metallic zinc); the solution of permanganate of potassa is then cautiously added drop by drop, until the pink colour appears, and the number of divisions of the burette required for the purpose accurately noted. The solution should be considerably diluted, and there must be a sufficient quantity of free acid present to keep in solution the peroxide of iron formed, and also the oxide of manganese. The whole of the iron must be at the *minimum* of oxidation, and the excess of sulphurous acid must be completely expelled: if the latter precaution be neglected an erroneous result will be obtained, as the sulphurous acid will itself take oxygen from the permanganic acid, and thus react in the same manner as iron.

To prepare the permanganate of potassa, 7 parts of chlorate of potassa, 10 parts of hydrate of potassa, and 8 parts of peroxide of manganese are intimately mixed. The manganese must be in the finest possible powder, and the potassa having been dissolved in water, is mixed with the other substances, dried, and the whole heated to very dull redness for an hour. The fused mass is digested with water, so as to obtain as concentrated a solution as possible, and dilute nitric acid added till the colour becomes violet; it is afterwards filtered through asbestos. The solution must be defended from the contact of organic matter, and kept in a glass stoppered bottle. If the solution be evaporated, it yields beautiful red acicular crystals. It is better to employ the crystals in the preparation of the test-liquor, as the solution keeps much better when no *manganate* is present. To prepare the normal or test-liquor, a certain quantity, say 5 grains of pianoforte wire, are dissolved in pure hydrochloric acid; after the disengagement of hydrogen has ceased, and the solution is complete, the liquor is diluted with about a pint of water, and accurately divided by measurement into two equal parts, the number of burette divisions of the solution of permanganate required to produce in each the pink colour is accurately noted, and this number is then employed to reduce into weight the result of the analysis of an ore. A useful normal liquor is made by dissolving 100 grains of the crystals in 10,000 grains of water.

(b.) *Penny's method.*—This is based on the reciprocal action of chromic acid and protoxide of iron, whereby a transference of oxygen takes place, the protoxide of iron becoming converted into peroxide, and the chromic acid into sesquioxide of chromium. The process is conducted as follows:—A convenient quantity of the specimen is reduced to coarse powder, and one-half at least of this is still further pulverized until it is no longer gritty between the fingers. The test solution of bichromate of potassa is next prepared, 444 grains of this salt, in fine powder, are weighed out, and put into a burette graduated into 100 equal parts; warm distilled water is afterwards poured in until the instrument is filled to 0. The palm of the hand is then securely placed on the top, and the contents agitated, by repeatedly inverting the instrument, until the salt is dissolved, and the solution rendered of uniform density throughout. Each division of the solution thus prepared contains 0·444 grain of bichromate, which Dr. Penny ascertained to correspond to half a grain of metallic iron. The bichromate must be pure, and should be thoroughly dried by being heated to incipient fusion. 100 grains of the pulverized ironstone are now introduced into a Florence flask with 1½ oz. by measure of strong hydrochloric acid and ½ oz. of water: heat is cautiously applied, and the mixture occasionally agitated, until all effervescence caused by the escape of carbonic acid ceases; the heat is then increased, and the mixture made to boil, and kept at a moderate ebullition for ten minutes or a quarter of an hour; about 6 oz. of water are next added, and mixed with the contents of the flask, and the whole filtered into an evaporating-basin. The flask is rinsed several times with water, to remove all adhering solution, and the residue on the filter is well washed. Several small portions of a weak solution of *red prussiate of potassa* (containing 1 part of salt to 40 of water) are now dropped upon a white porcelain slab, which is conveniently placed for testing the solution in a basin during the next operation. The prepared solution of bichromate of potassa in the burette is then added very cautiously to the solution of iron, which must be repeatedly stirred, and as soon as it assumes a dark greenish shade it should be occasionally tested with the red prussiate: this may easily be done by taking out a small quantity on the end of a glass rod and mixing it with a drop of the solution on the porcelain slab. When it is noticed that the last drop communicates a

distinct *blue* tinge, the operation is terminated; the burette is allowed to drain for a few minutes, and the number of divisions of the test liquor consumed, read off. This number multiplied by 2 gives the amount of iron per cent. The necessary calculation for ascertaining the corresponding quantity of protoxide is obvious. If the specimen should contain iron in the form of peroxide, the hydrochloric solution is deoxidized by sulphite of ammonia. The presence of peroxide of iron in an ore is easily detected by dissolving 30 or 40 grains in hydrochloric acid, diluting with water, and testing a portion of the solution with *sulpho-cyanide of potassium.* If a decided blood-red colour is produced, peroxide of iron is present. If it be desired to ascertain the relative proportions of peroxide and protoxide in an ore, two operations must be performed, one on a quantity of ore that has been dissolved in hydrochloric acid in a stout closed bottle, or in a flask through which a current of carbonic acid gas is maintained, and another on a second quantity that has been dissolved as usual and then deoxidized by sulphite of ammonia or by pure metallic zinc. It is advisable to employ the solution of bichromate much weaker than that proposed by Penny, and to employ a burette graduated to cubic millimètres—a good strength is 1 grain of metallic iron=10 cubic centimètres of bichromate.

Metals precipitable by Sulphuretted Hydrogen from the Hydrochloric solution.—A weighed portion of the ore, varying from 500 to 2000 grains, is digested for a considerable time in hydrochloric acid: the solution is filtered off; the iron in the filtrate reduced when necessary by sulphite of ammonia, and a current of sulphuretted hydrogen passed through it. The small quantity of sulphur (which is always suspended) is collected on a filter and thoroughly washed; it is then incinerated at as low a temperature as possible. The residue (if any) is mixed with carbonate of soda and heated upon charcoal before the blowpipe: any globules of metal that may be obtained are dissolved and tested.

Analysis of Pig Iron.—The most important constituents to be determined are *carbon* (combined and uncombined), *silicon, sulphur, phosphorus;* those of less consequence, or of more rare occurrence, are *manganese, arsenic, copper, zinc, chromium, titanium, cobalt, nickel, tin, aluminum, calcium, magnesium,* and the *metals of the alkalies.*

(1.) *Determination of the total amount of Carbon.*—About 100

grains of the iron in small pieces are digested, at a moderate temperature, in 6-oz. measures of a solution formed by dissolving 6 oz. of crystallized sulphate of copper, and 4 oz. of common salt in 20 oz. of water and 2 oz. of concentrated hydrochloric acid. The action is allowed to proceed until all, or nearly all the iron is dissolved. *Carbon and copper* are left insoluble; these are collected on a filter, and washed first with dilute hydrochloric acid (to prevent the precipitation of subchloride of copper), then with water, then with dilute caustic potassa, and finally with boiling water. The mixed carbon and copper are dried on the filter, from which they are easily removed by a knife-blade, and are mixed with oxide of copper, and burnt in a combustion tube in the usual way, with a current of air or, still better, of oxygen. The carbonic acid is collected in Liebig's apparatus, and from its weight the amount of carbon is calculated.

(2.) *Graphite*, or *Uncombined Carbon.*—A weighed portion of the finely divided iron (filings or borings may be used) is digested with moderately strong hydrochloric acid; the combined carbon is evolved in combination with hydrogen, while the graphite is left undissolved. It is collected on a filter, washed, and then boiled with a solution of caustic potassa, sp. gr. 1·27, in a silver dish; the silica which existed in the iron in the form of silicon is hereby dissolved; the clear caustic solution is drawn off by a pipe or siphon, and the black residue repeatedly washed; it is dried at as high a temperature as it will bear, and weighed; it is then heated to redness in a current of air, until the whole of the carbon is burnt off. A reddish residue generally remains, which is weighed, and the weight deducted from that of original black residue,—the difference gives the amount of graphite. This residue frequently contains *titanic* acid.

(3.) *Silicon.*—The amount of this element is determined by evaporating to dryness a hydrochloric solution of a weighed quantity of the metal: the dry residue is re-digested with hydrochloric acid, diluted with water, boiled and filtered; the insoluble matter on the filter is washed, dried, and ignited, until the whole of the carbon is burnt off; it is then weighed, after which it is digested with solution of potassa, and the residue, if any, washed, dried, ignited, and weighed: the difference between the two weights gives the amount of silicic acid, 100 parts of which indicate 47 parts of *silicon.*

(4.) *Phosphorus.*—A weighed portion of the metal is digested in nitro-hydrochloric acid, evaporated to dryness, and the resi-

due re-digested with hydrochloric acid. The solution is treated precisely as recommended for the determination of phosphoric acid in ores; every 100 parts of pyrophosphate of magnesia indicate 27·87 parts of phosphorus.

(5.) *Sulphur.*—In *grey* iron this element is very conveniently and accurately estimated by allowing the gas evolved by the action of hydrochloric acid on a weighed quantity (about 100 grains) of the metal, in filings or borings, to pass slowly through a solution of acetate of lead acidified by acetic acid: the sulphur, the whole of which takes the form of sulphuretted hydrogen, enters into combination with the lead, forming a black precipitate of sulphide of lead, which is collected, washed, and converted into sulphate of lead, by digesting it with nitric acid, evaporating to dryness, and gently igniting: 100 parts sulphate of lead=10·55 sulphur. The most minute quantity of sulphur in iron is detected by this process. If, however, crude *white* iron is under examination, this method does not give satisfactory results on account of the difficulty with which it is acted upon by hydrochloric acid; it is better, therefore, to treat the metal with nitro-hydrochloric acid, evaporate to dryness, re-digest with hydrochloric acid, and then precipitate the filtered solution with excess of chloride of barium; or the finely divided metal may be fused in a gold crucible with an equal weight of pure nitrate of soda and twice its weight of pure alkaline carbonates; the fused mass is extracted with water acidified with hydrochloric acid, and finally precipitated by chloride of barium. M. Nickles (Journ. de Pharm. et de Chimie) suggests the use of pure *bromine* mixed with distilled water as a solvent for cast iron or steel.

(6.) *Manganese.*—This metal is determined by the process described for its estimation in iron ores; the iron must exist in the solution in the form of sesquioxide.

(7.) *Arsenic and Copper.*—The nitro-hydrochloric solution of the metal is evaporated to dryness, re-digested with hydrochloric acid, and filtered. The iron in the clear solution is reduced to protochloride by boiling with a sufficient quantity of sulphite of ammonia; the solution is boiled till it has lost all smell of sulphurous acid. It is then saturated with sulphuretted hydrogen, and allowed to stand for twenty-four hours in a closed vessel, the excess of gas is boiled off, and the precipitate, if any, collected on a small filter and well washed; it is digested with monosulphide of potassium, which dissolves the sulphide of

arsenic, leaving the sulphide of copper untouched; the latter is decomposed by heating with nitric acid, and the presence of copper evinced by the addition of ammonia, which produces a fine blue colour; the sulphide of arsenic is precipitated from its solution in sulphide of potassium by dilute sulphuric acid; it may be redissolved in aqua-regia, and the nitric acid having been expelled by evaporation, the arsenic may be reduced in Marsh's apparatus. (See ARSENIC.)

(8.) *Nickel and Cobalt.*—These metals, if present, will be found in the solution from which the copper and arsenic have been precipitated by sulphuretted hydrogen. The solution is peroxidized, and the sesquioxide of iron precipitated by slight excess of carbonate of baryta, after which the nickel and cobalt are precipitated by sulphide of ammonium.

(9.) *Chromium and Vanadium.*—These metals, which should be looked for in the carbonaceous residue obtained by dissolving a large quantity of the iron in dilute hydrochloric or sulphuric acid, are detected as follows (Wöhler):—The ignited residue is intimately mixed with one-third of its weight of nitre, and exposed for an hour in a crucible to a gentle ignition. When cool, the mass is powdered and boiled with water. The filtered solution is gradually mixed and well stirred with nitric acid, taking care that it may still remain slightly alkaline, and that no nitrous acid is liberated which would reduce the vanadic and chromic acids. The solution is then mixed with an excess of solution of chloride of barium as long as any precipitate is produced. The precipitate, which consists of vanadate and chromate of baryta, is decomposed with slight excess of dilute sulphuric acid, and filtered. The filtrate is neutralized with ammonia, concentrated by evaporation, and a fragment of chloride of ammonium placed in it. In proportion as the solution becomes saturated with chloride of ammonium, *vanadate* of ammonia is deposited as a white or yellow crystalline powder. To test for chromium only, the mass after fusion with nitre is extracted with water, and then boiled with carbonate of ammonia; the solution is neutralized with acetic acid, and then acetate of lead added: the production of a yellow precipitate indicates *chromic* acid.

(10.) *Aluminum.*—This metal is best separated from iron, by first reducing the latter to the state of protoxide by sulphite of ammonia, then neutralizing with carbonate of soda, and afterwards boiling with excess of caustic potassa, until the precipi-

tate is black and pulverulent. The solution is then filtered off, slightly acidulated with hydrochloric acid, and the alumina precipitated by sulphide of ammonium.

(11.) *Calcium and Magnesium.*—These metals are found in the solution from which the iron and aluminum have been separated; they both exist probably (together with the aluminum) in the cast-iron in the form of *slag*, and are best detected in the black residue which is left on dissolving the iron in dilute sulphuric or hydrochloric acid. After digesting this residue with caustic potassa, and burning away the graphite, a small quantity of a red powder is left, which is composed of silicic acid, oxide of iron, alumina, lime, magnesia, and perhaps titanic acid; if 500 grains of cast-iron are operated upon, a sufficient quantity of insoluble residue will be obtained for a quantitative determination of its constituents. Moderately strong acid should be used, and no heat applied; it should be allowed to act on the iron for about a week, being repeatedly agitated.

(12.) *Determination of Carbon in Cast Iron and Steel.*—About 100 grains of the steel in small pieces are digested in 6-oz. measures of a solution of chloride of copper made by mixing 6 oz. of crystallized sulphate of copper, and 4 oz. of chloride of sodium with 20 oz. of water, and 2 oz. of concentrated hydrochloric acid. The mixture is warmed only, not heated so as to evolve hydrogen. The action is allowed to proceed until all, or nearly all, of the steel is dissolved. The residue, consisting of carbon and metallic copper, is collected on a filter and washed with dilute hydrochloric acid to prevent the precipitation of subchloride of copper, then with water, then with dilute caustic potassa, to ensure the removal of all the acid, and finally with water, it is then dried. The carbon and copper are easily removed from the filter by the blade of a knife, they are mixed with oxide of copper, and burnt in a combustion furnace with a current of air purified from carbonic acid by passing through solution of caustic potassa; the carbonic acid is collected as usual in Liebig's bulbs after drying by chloride of calcium. If *graphite* be present, it will be necessary to burn the carbon in a current of oxygen gas.

170. Uranium.

Oxide of Uranium is, according to Rose, completely precipitated from its acid solutions, having previously saturated them with ammonia, by the addition of sulphide of ammonium. No

inconvenience results from the solution containing any ammoniacal salts, except carbonate of ammonia and all alkaline carbonates. The precipitate is *black* or reddish-brown if the sulphide be greatly in excess. It is washed in water to which sulphide of ammonium is added. The precipitate is essentially protoxide of uranium, the composition of which is—

One equivalent of U	. . . .	60	. . 88·23
One ditto of O	. . . .	8	. . 11·77
One ditto of UO	. . .	68	. . 100·00

After being dried, it is ignited, to expel any little sulphur which may be retained: then it is calcined in a current of hydrogen at a high temperature, and left to cool in the gas. The protoxide is thus obtained pure. Should the solution contain much salts of potassa or of other strong non-volatile bases, the precipitate will retain a small quantity of these bases.

Separation of Oxide of Uranium from other metallic Oxides:—

(a.) *From those which are completely precipitated from their solutions by Sulphide of Ammonium.*

Add to the solution excess of carbonate of ammonia mixed with sulphide of ammonium; all the oxides which sulphide of ammonium transforms into sulphides are precipitated, whilst the protoxide of uranium is dissolved in the carbonate of ammonia. Leave the mixture to deposit in a closed vessel; wash the precipitate by decantation, with water containing carbonate of ammonia and sulphide of ammonium, and then filter. Gently heat the filtered liquid to expel most of the carbonate; decompose the sulphide with hydrochloric acid, oxidize the protoxide of uranium by nitric acid, precipitate the oxide by ammonia, and, before weighing, calcine in a current of hydrogen.

The tendency of the oxide of uranium to combine with bases, gives rise to its frequently carrying down along with it, in its precipitation by ammonia, bases which are not precipitated when alone, by that reagent, such as baryta and lime. If the liquid contain much potassa, a considerable quantity is often found in the precipitate, which is easily recognized by the orange-yellow colour perceptible at various parts of the heated precipitate. Sulphuretted hydrogen separates uranium from a great number of metals. The oxide may be separated very easily from the peroxide of iron by means of carbonate of ammonia; but those metals whose oxides dissolve in part, or wholly,

in carbonate of ammonia, such as *manganese*, *zinc*, *cobalt*, and *nickel*, have been regarded difficult of separation from uranium. The use of the carbonates of soda and of potassa affords a very exact and simple means of effecting their removal; for uranate of potash is not soluble in the carbonate of potassa, but it dissolves completely, and in very little time, in a liquid saturated with a bicarbonated alkali. When a solution of a salt of uranium is precipitated with a slight excess of carbonate of potassa, and the liquid diluted with water, the whole of the uranium is dissolved, and imparts to it a yellow colour. In both cases the double salt of potassa is formed. The carbonates of *zinc*, *cobalt*, and *manganese* are, on the contrary, insoluble in carbonate of potassa. To effect their separation, the solution may be thrown down, either by potassa, the precipitate being well washed and digested with bicarbonate of potassa, which will only dissolve the the oxide of uranium; or by slight excess of carbonate of potassa, the precipitate being collected on a filter, and washed as long as the liquor which passes through is coloured. On adding to a solution of the phosphate or arseniate of uranium, in an excess of carbonate of potassa, a known quantity of sesquioxide of iron dissolved in nitric acid, those two acids may be completely separated from the uranium, and their proportion determined by the increase in weight of the peroxide of iron. The oxide of uranium may also be separated by potassa, and the phosphoric and arsenic acids left in solution.

To separate the oxide of uranium in solution, it may be saturated with hydrochloric acid, boiled to expel the carbonic acid, and the uranium precipitated by ammonia; but as the liquor contains much potassa, the precipitate retains a certain quantity, and is not entirely converted into the state of green oxide, which makes it necessary to redissolve it, and precipitate again with ammonia.

To extract uranium with great precision from the uranate of potassa dissolved in hydrochloric acid, the whole is evaporated to dryness in a platinum crucible, gradually heated, and a current of dry hydrogen conveyed into it, as long as the gas which is given off possesses an acid reaction. The double chloride of potassium and uranium is converted into uranium (so called) in the form of a black powder, which is separated by washing from the chloride of potassium.

(b.) *Separation from Nickel, Cobalt, and Zinc.*—When the oxide of uranium in its preparation from *pitchblende* is so far

purified as to be dissolved in carbonate of ammonia, Wöhler directs to mix sulphide of ammonium with the solution as long as a black precipitate falls; in this way the nickel, cobalt, and zinc are entirely separated, no uranium being precipitated. According to Berthier, *uranium* is completely separated from *iron*, *manganese*, *cobalt*, *nickel*, and *zinc*, by boiling the solution after the addition of sulphite of ammonia.

(c.) *From Oxide of Iron* (Pisani).—As oxide of uranium, dissolved in carbonate of ammonia, is not precipitated by ammoniacal sulphide, we have only to add to the liquid separated by filtration with the oxide of iron, several drops of the latter reagent, to eliminate from it in the state of sulphide the small quantity of iron which has been dissolved; after filtering we get a liquid containing all the uranium without any trace of iron.

Analysis of Pitchblende.—Of the various methods which have been employed by different chemists, the following, adopted by Arfwedson, seems on the whole the best. The mineral is reduced to fine powder, and digested with boiling aqua-regia; the solution is evaporated on a water bath, to expel the excess of acid, then diluted with water, and precipitated by sulphuretted hydrogen, sulphurous acid being previously added to reduce the arsenic acid to arsenious acid: *arsenic*, *copper*, *lead*, and *bismuth* are in this manner precipitated. The solution is filtered, the excess of sulphuretted hydrogen expelled by boiling, and ammonia added: the precipitate thereby formed is washed and dissolved, while yet moist, in carbonate of ammonia, peroxide of iron remains undissolved, and is separated by filtration. The solution is evaporated till the ammonia is volatilized, whereupon the peroxide of uranium is rendered insoluble; it is washed, dried, and calcined in a platinum crucible, by which it becomes converted into *urano-uranic oxide* of a green colour. The uranates of lime, zinc, cobalt, or nickel, which may have been present in the solution, are not decomposed by the calcination; they are readily dissolved, however, by dilute hydrochloric acid, which acid serves therefore to separate them from the urano-uranic oxide, which is thus obtained pure. It is washed first with dilute acid, and then with distilled water.

From the metallic uranates in solution in hydrochloric acid, oxide of uranium may be obtained. For this purpose the solution is precipitated by ammonia, the dried precipitate is reduced by

hydrogen gas, and treated immediately with hydrochloric acid, which dissolves all the foreign metals, leaving protoxide of uranium insoluble.

Another method (Kessler).—The mineral is dissolved in nitric acid, water added, and sulphuretted hydrogen passed into the solution at the temperature of about 86° F., to separate *arsenic, copper*, and *lead*. The iron in the liquid is then again oxidized either by chlorine or by hot nitric acid, tartaric acid is added, the fluid is saturated with ammonia, when everything remains in solution. Bicarbonate of ammonia well saturated with carbonic acid is then added, the solution is next submitted again rapidly to the action of sulphuretted hydrogen as long as a precipitate is formed; sulphides of *zinc, iron, nickel*, sometimes *cobalt*, are separated, whilst the oxide of uranium remains in solution. These solutions are washed with a dilute solution of bicarbonate of ammonia saturated with carbonic acid, and containing sulphuretted hydrogen.

During the passage of the sulphuretted hydrogen through the tartaric acid fluid, care must be taken to maintain an excess of carbonic acid, which is liable to be displaced by sulphuretted hydrogen, and which prevents the oxide of uranium from becoming converted into sulphide, and the other metallic sulphides from forming green sulphur-salts, and passing through the filter. This is easily done by adding some fragments of marble to the sulphide of iron employed in furnishing the sulphuretted hydrogen.

To extract uranium from pitchblende, Liebig directs to heat the mineral to redness, then reduce it to an impalpable powder, and digest with nitric acid diluted with four parts of water, taking care to employ a larger quantity of mineral than the acid can dissolve. By this process, the protoxide of uranium is converted into sesquioxide, which unites to the nitric acid almost to the total exclusion of the iron. Sulphuretted hydrogen is then transmitted through the solution, by which *copper, lead*, etc., are separated. The solution is boiled to expel any free acid, and after being concentrated by evaporation, is set aside to crystallize. Nitrate of uranium crystallizes in lemon-coloured flattened prisms.

171. Manganese.

This metal is quantitatively estimated as *protoxide*, as *red oxide*, or as *protosulphate*, and as *sulphide*.

Quantitative estimation as Protoxide.—Ebelmen prefers reducing the higher oxides of manganese to the state of protoxide for the purpose of weighing. To perform the experiment, he introduces the oxide into a small platinum crucible, the lid of which has a small platinum tube in the centre, through which a current of dry hydrogen gas is conveyed by means of a glass tube, of a diameter nearly equal to that in the crucible cover; heat is applied by means of a spirit lamp; the reduction is complete after a few minutes, and a rapid current of gas is passed into the crucible while cooling; the oxide obtained is quite pure, it dissolves in hydrochloric acid without rendering it black, and without disengaging chlorine. Its composition is—

One equivalent of Mn	27·5	77·5
One ditto of O	8·0	22·5
One ditto of MnO	35·5	100·0

Quantitative estimation as Red Oxide.—The solution is heated to boiling with excess of carbonate of soda. Should ammoniacal salts be present, the solution must be treated in the same manner as in the precipitation of carbonate of zinc, under similar circumstances; the precipitate is thoroughly washed, dried, and ignited, by which it is decomposed into the red oxide (manganoso-manganic oxide); sometimes the solution is precipitated with caustic potassa, and the hydrated protoxide thus formed is converted into red oxide by strong ignition; it must be remembered, however, that hydrated protoxide of manganese is soluble in sal-ammoniac. It is sometimes convenient also to precipitate manganese as sulphide by adding coloured sulphide of ammonium to the solution to which sal-ammoniac and ammonia have been added; the precipitate, having been washed with water containing sulphide of ammonium, is digested with hydrochloric acid, and the solution precipitated by carbonate of ammonia. The composition of red oxide of manganese is—

Three equivalents of Mn	82·5	72·05
Four ditto of O	32·0	27·95
One ditto of $MnO + Mn_2O_3$	114·5	100·00

Quantitative estimation as Sulphate.—Oxide of manganese is converted into protosulphate in the same manner and with the same precautions as magnesia; the salt must be ignited very

feebly, or it will lose sulphuric acid. Its composition is—

One equivalent of MnO . .	35·5 . .	47·20
One ditto of SO_3 . .	40·0 . .	52·80
One ditto of MnO,SO_3	75·5 . .	100·00

Quantitative estimation as Sulphide.—In the absence of ammoniacal salts, manganese is completely precipitated from its solutions by sulphide of ammonium. The dried sulphide is introduced into a crucible mixed with a little sulphur. The crucible is provided with a perforated cover, through which a current of dry hydrogen gas is passed. When the crucible is full of hydrogen, heat is applied for some time, the crucible is then allowed to cool whilst the gas continues to pass, at the bottom of the crucible a mass of sulphide (MnS) is found, which, when not much heated, is green and black, like the native sulphide when red-hot. The sulphate, and all the oxides of manganese, can, according to Rose, be thus converted into a sulphide of invariable composition.

Separation of Oxide of Manganese from the Oxides of the Fourth, Third and Second Groups.

(a.) *From Oxides of Cobalt and Nickel.*—Rose's original method, which, though complicated, gives very accurate results, is the following:—The metals are first precipitated together as oxides by caustic potassa, they are then ignited, weighed, and converted into chlorides by introducing them into a bulbed tube, and transmitting over them a current of dry hydrochloric acid gas, a moderate heat being at the same time applied; it requires a long time thus to convert the oxides completely into chlorides; when the conversion is complete, dry *hydrogen gas* is passed through the apparatus, the bulb containing the chlorides being strongly heated, the hydrogen displaces the chlorine from the chlorides of cobalt and nickel, forming with it hydrochloric acid gas; and the operation must be continued as long as white clouds are formed, on holding a glass rod that has been dipped in ammonia at the end of the apparatus where the excess of gas escapes. The hydrogen is allowed to pass through the tube till it is quite cold, the chloride of manganese, which has not been decomposed by the process, is dissolved out by water, the reduced cobalt and nickel are washed with very dilute hydrochloric acid, and, finally, with water; the two metals are then separated from each other by one of the methods above given, and the manganese is precipitated from the solution of

the chloride, to which have been added the washings from the cobalt and nickel by carbonate of soda.

Rose states that *nickel* may be conveniently separated from manganese in the same manner as cobalt, namely, by chlorine and carbonate of baryta. A method of separating oxide of cobalt from oxide of manganese was proposed by Barreswil; it consists in adding carbonate of baryta to the solution, and then passing a current of sulphuretted hydrogen through it, by which, according to Barreswil, cobalt only is precipitated: this method has not, however, been found successful by other chemists. A plan for the separation of oxides of cobalt and nickel from oxide of manganese was proposed by Wakenroder, and has obtained the approval of Rose; it is based on the fact that, although nickel and cobalt are not precipitated from their acid solutions by sulphuretted hydrogen, their sulphides precipitated by sulphide of ammonium are *not* dissolved by very dilute hydrochloric acid. The acid solution of the three oxides is made ammoniacal, and the metals are precipitated by sulphide of ammonium, the solution is then rendered slightly acid by dilute hydrochloric acid; the sulphide of manganese is dissolved with facility, small portions also of the sulphides of cobalt and nickel may also be dissolved, but they may be removed by precipitating the solution with ammonia and sulphide of ammonium, and treating it anew with dilute hydrochloric acid.

From Cobalt (Liebig's method).—The metals are precipitated by cyanide of potassium, an excess of which redissolves the cyanide of cobalt, and a part also of the protocyanide of manganese, while another portion remains undissolved; this is filtered off and washed; the filtrate is heated to ebullition, a few drops of hydrochloric acid, insufficient, however, to acidify the solution, are added from time to time, and the manganese and cobalt are separated from one another in the same manner as nickel is separated from cobalt.

Ebelmen has recently proposed to separate manganese from cobalt or nickel, by exposing the mixture of the oxides in a platinum or porcelain tray to a current of dry sulphuretted hydrogen, at a temperature a little below redness. The oxides are converted into sulphides, the sulphide of manganese is dissolved by very weak hydrochloric acid, in the cold, and after filtration is precipitated at a boiling heat by potassa, and the sulphide of cobalt remaining on the filter is redissolved in nitric acid, and precipitated by caustic potassa. The smallest quantity

of cobalt may, he says, be detected in this manner. He applies the same process to the separation of arsenic from tin.

From Iron and Nickel (Schiel).—A stream of chlorine is passed through the solution to which acetate of soda has been added, peroxide of manganese is precipitated, the nickel and iron remaining in solution. If cobalt be present, it is separated as oxide.

(b.) *From Oxide of Zinc.*—The oxides are dissolved in excess of acetic acid, and the zinc is precipitated by sulphuretted hydrogen; the solution must be acid, and contain no other acid but acetic.

Another method (Flajolot).—The excess of acid in the solution is neutralized by carbonate of soda; an excess of cyanide of potassium is then added, and afterwards carbonate of soda. At the temperature of ebullition, carbonate of manganese is precipitated alone.

(c.) *From Oxide of Chromium.*—This is effected in the same manner as the separation of oxide of zinc from oxide of chromium.

(d.) *From Alumina* (Rose).—Add chloride of ammonium, heat to ebullition; pour in caustic ammonia and boil until the excess of the latter is disengaged; the alumina will then be completely precipitated and perfectly free from manganese, even when operating with free access of air.

(e.) *From Magnesia and Lime.*—Add a solution of acetate of soda, heat, and pass a current of chlorine through the liquid, when permanganate will be formed. Supersaturate with ammonia and boil, upon which all the manganese is reduced to sesquioxide and precipitated, the magnesia and lime remaining in solution. If the quantity of magnesia be large, a certain quantity of chloride of ammonium must first be added.

Determination of the value of Commercial Binoxide of Manganese:—

(1.) By estimating the amount of chlorine evolved during the solution of the ore in hydrochloric acid; the value of the oxide being in exact proportion to the quantity of chlorine produced.

Three methods of estimating the chlorine have been employed.

(a.) *By noting the quantity of Protosulphate of Iron which it peroxidizes.*—If the oxide of manganese be perfectly pure, 4·35 parts (one equivalent) will produce 35·5 parts (one equivalent) of chlorine, which will peroxidize 278 parts (two equivalents) of crystallized protosulphate of iron.

Hence 25 grains of pure oxide of manganese yield chlorine sufficient to peroxidize 159 grains of protosulphate of iron; 25 grains of the powdered specimen are weighed out, and a quantity not less than 359 grains of crystallized protosulphate of iron. The oxide of manganese is thrown into a flask containing about one ounce of strong hydrochloric acid slightly diluted, and a gentle heat applied. The protosulphate of iron is gradually added in small quantities to the acid, so as to absorb the chlorine as it is evolved, and the addition of that salt continued till the liquor, after being heated, gives a *blue* precipitate with *ferridcyanide of potassium*, and has no smell of chlorine, which are indications that the protosulphate of iron is present in excess; by weighing what remains of this salt, the quantity that has been added is ascertained, say *m* grains. If the whole of the specimen consisted of peroxide, it would require 159 grains of protosulphate of iron, and that quantity would therefore indicate 100 per cent. of peroxide; but, if a *portion* of the manganese only is peroxide, a proportionally smaller quantity of the protosulphate will be consumed, and that quantity will give the real proportion of peroxide, by the proportion, as 159 : 25 : : *m* to the quantity required.

(b.) The chlorine evolved is passed through water in which *lime* is diffused; *chloride of lime* is formed; a certain quantity of protosulphate of iron is dissolved in water, and the solution of chloride of lime is added thereto, until the iron liquor ceases to strike a blue colour with a drop of solution of red prussiate of potassa: then, comparing the quantity of the solution of chloride of lime required, with the quantity that was produced, the quantity of chlorine generated, and hence the total quantity of available oxygen, is known.

(c.) Baumann conveys the chlorine into a solution of nitrate of silver, and calculates the amount of real peroxide of manganese in the specimen from the quantity of chloride of silver formed.

(2.) *By converting Oxalic Acid into Carbonic Acid, by means of the second atom of Oxygen which the Peroxide of Manganese contains.*—$MnO_2 + C_2O_3$, producing MnO, and $2CO_2$. 100 grains of the specimen are introduced into a weighed flask, and 150 grains of oxalic acid dissolved in 500 grains of water are poured upon it; to this, 350 grains of oil of vitriol are to be added, and the orifice of the flask closed by a cork, through which passes a tube containing fragments of recently fused chloride of cal-

cium ; the weight of this cork and tube are to be included in the tare of the flask. On the addition of the oil of vitriol, a brisk effervescence takes place, owing to the escape of carbonic acid, which passing over the fragments of chloride of calcium in the tube is dried, so that the gas alone passes off. When the action slackens, a gentle heat may be applied, until all the oxide of manganese has dissolved; the small quantity of a light brownish sediment, which generally falls, is easily distinguished from the particles of black oxide. As soon as the action is quite over, the flask is allowed to cool, and as it still contains a quantity of carbonic acid gas, this is removed by taking out the cork, and blowing air gently into the flask by a glass tube; the cork is then to be replaced, and the flask with its contents weighed; the difference of weight represents the amount of carbonic acid evolved, *one-fourth* of the oxygen of which had been derived from the peroxide of manganese by its conversion into protoxide, which remains combined with sulphuric acid in the liquor, and the quantity of peroxide in the 100 grains of the one are thus directly found. *Example.*—Suppose the flask and the materials together to weigh 1876 grains, and after the action has terminated 1816·5 grains: the loss, 59·5 grains, is carbonic acid, consisting of 16·3 grains of carbon, and 43·2 grains of oxygen; the oxygen derived from the mineral is therefore $\frac{43{\cdot}2}{4} = 10{\cdot}8$, which represents 59 grains of pure peroxide of manganese in 100 grains of the substance experimented upon.

(3.) *Method of Fresenius and Will.*—This is founded on the same principle. A certain weighed quantity of the finely powdered manganese ore is projected into B (see Fig. 69, p. 268), and about $2\frac{1}{2}$ parts of *neutral oxalate of potassa*, prepared by saturating the common binoxalate with carbonate of potassa and crystallizing, or two parts of neutral oxalate of soda, and as much water added as will fill about one-third of the flask; the apparatus is then prepared as directed in p. 269, B is then closed, the apparatus weighed, and, by sucking the tube *e*, some sulphuric acid is made to pass from *a* into *b*. The evolution of carbonic acid commences immediately, and in a very uniform manner: as soon as it stops, some more sulphuric acid is sucked over from *a* into *b*, and the operation thus continued till all the manganese is completely decomposed: this operation will require from six to ten minutes: its completion is ascertained not only by no further evolutions of carbonic acid taking place upon a further influx

of sulphuric acid into *b*, but also by no black powder remaining at the bottom of the flask. Some more sulphuric acid is then sucked over into *b*, in order to heat the fluid contained therein, so as completely to expel all the carbonic acid evolved during the course of the operation; the wax stopper is then removed from *a*, and the tube *d* sucked until the air no longer tastes of carbonic acid; the apparatus is then allowed to cool, and weighed. The entire examination may thus, according to the authors, be performed in a quarter of an hour; from the loss of weight of the apparatus (the amount of carbonic acid expelled) the amount of available oxygen is found, or, what in fact is the same, the amount of peroxide contained in the manganese under examination, according to the following arrangement. *Two* equivalents of carbonic acid stand to *one* equivalent of peroxide of manganese in the same proportion as the amount of carbonic acid found stands to x, x being the quantity of real peroxide contained in the specimen. Let us suppose that our experiment had been made with four grammes (61·76 grs.) of manganese ore, and that we had obtained 3·5 grammes (54·03 grs.) of carbonic acid. The arrangement would be—

$$4 : 43{\cdot}67 : : 3{\cdot}5 : x$$
$$x = 3{\cdot}47.$$

Thus, four grammes of the manganese ore containing 3·47 grammes of peroxide, 100 parts of the same substance must contain 86·7 parts. To render, however, this calculation unnecessary, we need only ascertain what amount of manganese must be taken to make the number of centigrammes of carbonic acid obtained immediately indicate the percentage amount of peroxide. The calculation must therefore be—

$$4 : 43{\cdot}67 : : 100 : x$$
$$x = 0{\cdot}993.$$

Thus, if we take 0·993 grammes (15·33 grains) of the specimen, the number of centigrammes of carbonic acid expelled will indicate the percentage amount of peroxide. But as the quantity of carbonic acid obtained would be too minute to admit of a direct determination of its weight, it is advisable to take a multiple of 0·993 grammes, and to divide the number of centigrammes of carbonic acid obtained by the same number, which has served as a multiplier. The multiple by 3, *i.e.* 2·98 grammes, is deemed by the authors the quantity best adapted for the examination. Should the manganese contain carbonated alkaline earths, which is sometimes the case, it must undergo a

preliminary process previous to the examination. To ascertain the presence or absence of carbonate of lime or baryta in the manganese under examination, it is sufficient to moisten a sample powder with dilute nitric acid; their presence is certain if any effervescence take place. The specimen, in that case, is treated as follows:—2·98 grammes of the specimen are projected into *b*, covered with very dilute nitric acid, one part acid to twenty parts of water, and allowed to stand at rest for a few minutes; the supernatant fluid is then poured upon a small paper filter, the manganese remaining in the flask is repeatedly washed with water, as well as the solid particles on the filter, (the supernatant water being always poured on the filter), and the latter then thrown into *b*, taking care not to lose a particle of manganese; the further operation is conducted as usual. The neutral oxalate of potassa is preferable to free oxalic acid, or to binoxalate of potassa, since, when employing the former substance, the evolution of carbonic acid commences only upon the influx of sulphuric acid into *b*, whilst free oxalic acid, or binoxalate of potassa, begin to evolve carbonic acid immediately upon coming into contact with manganese and water; and this would, of course, interfere with the correctness of the results, rendering it almost impossible to determine the exact weight of the apparatus before the commencement of the operation. Such is the method of examining ores of manganese proposed by the German chemists: the results are most accurate, and the manipulation is so simple, that it will no doubt entirely supersede all the other methods that have been described. It will be observed that, from the almost absolute identity of the equivalent number of carbonic acid multiplied by 2, $22 \times 2 = 44$, with that of peroxide of manganese, 43·67, the calculation of the quantity of real peroxide in a specimen of manganese becomes a problem of the utmost simplicity; and that, if we take 100 grains of the specimen, the loss of weight in *grains* will denote the percentage proportion of pure peroxide. One atom of peroxide of manganese, $MnO_2 = 43{\cdot}67$, contains one atom of oxygen, separable by sulphuric acid, and capable of converting one atom of oxalic acid into two atoms of carbonic acid. Thus:—

Oxalic Acid, $C_2O_3 + O = 2CO_2$
Ditto . . $36 + 8 = 44$

Dr. Ure recommends 250 grains of oxalate of potassa to 100 grains of the sample.

Various other methods of ascertaining the value of commercial oxide of manganese have been proposed; but as none of them exceed in accuracy or convenience the method of Will and Fresenius just described, the principles of the processes alone will be briefly described.

(4.) *Method founded on the reducing action of Protochloride of Tin* (L. Müller, Ann. der Chem. und Pharm., Oct. 1851, and Chem. Gaz., vol. x. p. 75).

Protochloride of tin and perchloride of iron react mutually on each other, thus—

$$SnCl + Fe_2Cl_3 = SnCl_2 + 2FeCl.$$

In order to derive advantage from this reaction, two courses might be followed: first, a solution of protochloride of iron might be converted into perchloride by the action of the chlorine developed from hydrochloric acid by the oxide of manganese to be valued, and then the quantity of perchloride of iron thus formed in this solution, determined by means of a solution containing a known proportion of protochloride of tin; or secondly, the chlorine evolved may be passed through a solution of protochloride of tin, and the perchloride produced estimated by means of a solution of perchloride of iron of known strength. The author finds the second method to be perfectly applicable in practice, as the chlorine is rapidly and completely absorbed by a solution of protochloride of tin.

(5.) *Method founded on the conversion of Arsenious Acid into Arsenic Acid by means of Chlorine and Permanganate of Potash* (Astley Price, Chem. Gaz., vol. ii. p. 416).

Ten or any number of grains of the specimen under examination are placed in a small flask, to which ten or more measures of a normal solution of arsenious acid in hydrochloric acid are added, and to the flask is adapted a Will's nitrogen apparatus, containing a solution of potassa, to retain any terchloride of arsenic which may be given off. The flask is then placed in a water-bath, or a gentle heat is applied until solution is effected. The contents of the flask, after being allowed to cool, are, together with the solution of potassa, transferred to a larger flask and diluted with water. The amount of arsenious acid remaining unchanged, is then determined by the addition of a standard solution of permanganate of potassa, and the quantity thus indicated being deducted from the number of grains of arsenious acid employed in the first instance, will give the value of the specimen under analysis.

(6.) *Method founded on the conversion of Copper into Dichloride by the Chlorine evolved from Hydrochloric Acid by Oxide of Manganese* (Nolte, Chem. Gaz., vol. xvii. p. 296).

Every atom of peroxide in the ore sets free one atom of chlorine from hydrochloric acid, which in its turn converts two atoms of copper into dichloride. Strong chemically pure hydrochloric acid is poured over a known quantity of the native peroxide in a retort, and an excess of copper is added, the evolution of free chlorine being avoided by keeping the retort as cool as possible until the ore is completely decomposed. The mixture is then heated to the boiling-point, so as to convert the protochloride at first formed into dichloride. The loss of copper in weight, gives the amount of peroxide in the ore, since every two atoms of copper dissolved answer to one of peroxide.

GROUP V.—Section A.

Lead, Thallium, Silver, Mercury, Bismuth, Cadmium, Copper, Palladium, Rhodium, Osmium, Ruthenium, Iridium.

172. Lead.

This metal is completely precipitated from its acid solutions by *sulphuretted hydrogen;* it is also precipitated by *sulphuric acid*, by *carbonate of ammonia*, by *oxalate of ammonia*, by *hydrochloric acid*, and by *bichromate of potassa;* and it may therefore be weighed as *sulphide*, *sulphate*, *chloride*, *chromate*, and as *oxide*, the latter being produced by igniting with free access of air, the carbonate and oxalate. Lead is likewise estimated by volumetric processes.

Precipitation as Sulphide.—A stream of washed sulphuretted hydrogen gas is transmitted through the solution, rendered slightly acid with nitric acid until it is completely saturated, a gentle heat is then applied, and the precipitated sulphide is filtered as quickly, and with as little access of air, as possible, in order to avoid the decomposition of a portion of the sulphuretted hydrogen, which would occasion a precipitation of sulphur; as it is difficult, even with great care, to prevent this, it is better to convert the washed sulphide of lead into sulphate, which is done by transferring it, filter and all, into a beaker, and pouring on it concentrated and fuming nitric acid, the

sulphur becomes hereby oxidized into sulphuric acid; a gentle heat is applied to assist the action; the mixture is carefully transferred into a small Berlin crucible, and a few drops of sulphuric acid being added, it is evaporated to dryness and ignited. The composition of sulphate of lead is—

One equivalent of PbO . .	111·5 . .	73·60
One ditto of SO_3	40·0 . .	26·40
One ditto of PbO,SO_3 . .	151·5 . .	100·00

With respect to the precipitation of lead by sulphuretted hydrogen, the following observations have been made by Dr. Vogel. In precipitating lead with sulphuretted hydrogen it is usual to warm the liquid, to prevent any of the precipitate from passing through the filter, but this may give rise to considerable loss. If sulphuretted hydrogen be passed through a moderately strong solution of acetate of lead, until the filtered liquor contains no more metal, and is consequently not rendered turbid either by sulphuretted hydrogen or by sulphuric acid, and if the liquor be now warmed, a further precipitate is produced by sulphuretted hydrogen after filtration; the liberated acetic acid evidently decomposes the sulphide of lead. The same is the case with nitrate of lead, and remarkably so with the chloride. This is of considerable importance where lead has to be separated from chlorides, and where it cannot be precipitated by sulphuric acid. With *mercury* and *bismuth* no such decomposition of the sulphide occurs, and only in a slight degree with *antimony*. The above behaviour may even be employed for the separation of some metals. If, for example, sulphuretted hydrogen be passed into a liquid containing *nitrate of bismuth* and *nitrate of lead*, until no further precipitate occurs, and the whole be then heated to boiling, the sulphide of lead is entirely redissolved, while the sulphide of bismuth is not attacked. The lead may then be precipitated from the solution by sulphuric acid. According to Rose, lead may be quantitatively estimated as sulphide by heating the washed precipitate by sulphuretted hydrogen in contact with sulphur in a crucible through which a current of sulphuretted hydrogen is made to pass. The heat should be a full red, and the sulphide (PbS) should be perfectly crystalline.

Volumetric estimation of Lead by Sulphide of Sodium.—A method of estimating lead by means of a normal solution of sulphide of sodium was proposed by Domonté, and is de-

scribed by him as simple, quick, and accurate, and well adapted for the examination of *white lead* and *acetate of lead*, substances which, as met with in commerce, are often greatly adulterated. To prepare the normal solution of sulphide of sodium, about 300 grains are dissolved in a pound of water, a certain known quantity of lead is dissolved in nitric acid, precipitated, and redissolved by caustic potassa; the solution of sulphide of sodium placed in a graduated burette, is added carefully to the alkaline solution, which is maintained at a temperature near to ebullition. Each addition of the sulphide produces a black precipitate of sulphide of lead; from time to time the liquid is boiled, and the precise point at which a drop of the reagent produces no further precipitate is carefully observed. The number of divisions of the burette which have been required represents the value of the lead employed in the experiment: thus, suppose 10 grains of lead to have been used, and 30 burette divisions of the alkaline sulphide have been required, then, in all analyses of commercial products, for every 30 divisions of the burette that are required the operator may infer that 10 grains of lead are present.

The author does not find the success of the experiment to be interfered with by the presence of *tin*, *antimony*, *arsenic*, *iron*, *cobalt*, *nickel*, or *zinc*. The first three metals are not precipitated by an alkaline sulphide; in the presence of excess of free alkali, *zinc* is precipitated *after* the lead, but the colour of the sulphide being white, renders its presence rather an advantage than otherwise; *copper* complicates the process. It is necessary in the first place to determine this metal by one of the methods to be described hereafter. Domonté then makes a synthetic essay on a mixture formed of a weight of copper equal to that found by experiment, and of lead equal in weight to that employed in preparing the standard solution. This assay shows by how many divisions the plumbimetric liquor ought to be diminished, on examining the alloy. The number is, in fact, the difference between the results of the assay of pure lead, and those of the assay of the mixture of lead and copper. This being done, he examines the alloy in the ordinary way. *Bismuth* cannot be separated from lead in this way, but, commercially speaking, it is not likely that this metal will be found to occur as a contamination, its higher price being a guarantee.

Volumetric estimation of Lead by Bichromate of Potassa

(Schwarz; Dingler's 'Polytechnisch Journal').—A standard solution of bichromate is formed by dissolving 14·730 grammes of the pure salt in sufficient water to form one litre. One cubic centimètre of this solution precipitates 0·0207 gramme of lead. The lead to be analysed is dissolved in the minimum of nitric acid, the solution diluted with water, carefully neutralized with carbonate of soda or with ammonia, an excess of acetate of soda added, and the solution precipitated by the bichromate of potassa solution. When the precipitation approaches its end, or when the precipitate commences readily to subside, some drops of a neutral solution of *nitrate of silver* are deposited on a porcelain plate, and the chromate solution only, added by two or three drops at a time, to the liquid under examination; after each addition, the whole is well stirred, allowed to subside, and a drop of the clear supernatant liquor added to one of the drops of the silver solution. As soon as the bichromate is in excess, a *red* colour is produced, while the precipitated chromate of lead has no effect on the silver test, but simply floats on the top as a yellow precipitate. It is only now necessary to read off the number of divisions of the burette that have been required, to learn the amount of lead in the solution. The operator must be careful to add abundance of acetate of soda. The only foreign metal which, according to the author, interferes with the reaction, is *bismuth*, in the presence of which it is inapplicable.

Quantitative estimation as Sulphate.—When lead is to be weighed in the form of this salt, the solution is precipitated by dilute sulphuric acid, and then mixed with twice its volume of alcohol, sulphate of lead not being altogether insoluble in water; it is collected on a filter, on which it is washed with spirits of wine. Its composition has been given above. According to Vogel, sulphate of lead precipitated from solutions containing nitric acid, is never free from that acid, and when lead is thrown down by sulphuretted hydrogen from compounds containing *zinc*, the sulphide of lead always contains sulphide of zinc.

Quantitative estimation as Oxide:—

(a.) *Precipitation as Carbonate.*—Carbonate of ammonia, mixed with a little caustic ammonia, is the precipitant employed, and the solution is heated; it is washed on the filter with pure water, and afterwards ignited in a porcelain crucible, by which it is converted into protoxide of lead. The pre-

cipitate is removed as completely as possible from the filter and the latter is ignited alone, the residue being afterwards mixed with the ignited precipitate; the object of this is to prevent the reduction of a portion of the protoxide of lead by the organic matter of the filter. The same observation applies to the sulphate.

(b.) *Precipitation as Oxalate.*—Rose prefers *oxalate of ammonia* as the precipitant of oxide of lead from its solutions, which must be either neutral or weakly ammoniacal. The precipitated oxalate of lead is converted into protoxide by ignition in an open porcelain crucible, having, as in the two former cases, been removed as much as possible from the filter, the latter being ignited alone.

The composition of protoxide of lead is—

One equivalent of Pb . . .	103·50 . .	92·83
One ditto of O . . .	8·00 . .	7·17
One ditto of PbO . .	111·50 . .	100·00

Quantitative estimation as Chloride.—The solution is precipitated by excess of hydrochloric acid, concentrated by evaporation on the water-bath, and the residue washed with absolute alcohol, mixed with ether. As chloride of lead is volatilizable, it must not be ignited, but dried at a temperature below redness. Its composition is—

One equivalent of Pb . . .	103·50 . .	74·46
One ditto of Cl . . .	35·50 . .	25·54
One ditto of PbCl . .	139·00 . .	100·00

Estimation of Lead in small quantities in the presence of other metals, by precipitation as Chromate.—There are frequent instances in which the chromate of potassa offers considerable advantages as a precipitant of lead, and the efficacy of this reagent is increased by the great insolubility of chromate of lead, particularly in acetic acid, it may therefore be employed to precipitate this metal in the presence of copper and zinc. The chromate of lead precipitated should be dissolved in a little hot dilute hydrochloric acid; a small crystal of tartaric acid added, and the solution, rendered alkaline by ammonia, should be treated with hydrosulphuric acid, or mixed with sulphide of ammonium. The sulphide of lead thus obtained is washed, and converted into sulphate by the usual method.

Analysis of Galena.—Treat the pulverized mineral with concentrated nitric acid; evaporate to dryness with a small excess of sulphuric acid; treat the dry mass with water, which dissolves out all the sulphates but that of lead. *Tin*, *antimony*, *quartz*, and *sulphate of baryta* would, if present, be left in the insoluble portion. Collect and weigh the insoluble portion; digest it repeatedly with acetate of ammonia (sp. gr. 1·065), wash, dry, and weigh. The difference indicates the amount of sulphide of lead. The lead may be precipitated from its solution in acetate of ammonia by sulphide of ammonium, and the sulphide of lead may be oxidized into sulphate by nitric and sulphuric acids.

From all the metals that have hitherto been treated of, lead may be separated by sulphuretted hydrogen; the solution should be acidified by nitric acid, and considerably diluted.

Separation of Sulphate of Lead from Sulphate of Baryta.—Hyposulphite of soda dissolves sulphate of lead. To effect the separation, a concentrated solution of the hyposulphite is added to a mixture of the two salts, and the whole gently warmed, taking care that the temperature does not exceed 68°; at a higher temperature sulphite of lead is formed, which is insoluble in the hyposulphite.

173. Protoxide of Thallium.*

General Characters.—This oxide may be prepared by allowing granulated thallium to oxidize in warm, moist air, and then boiling in distilled water. By repeating this operation two or three times, a saturated hot solution of the oxide is formed. Upon filtering, the small quantity of carbonate which may have formed, separates at first in white needles, whilst upon further cooling the oxide crystallizes out in yellow needles.

Anhydrous protoxide of thallium is formed by exposing these yellow crystals in a vacuum over sulphuric acid; it then forms a reddish-black mass, retaining the shape of the crystals. When heated to about the melting-point of the metal, it melts to a brown, limpid liquid, which at a high temperature evolves reddish-black vapours, partially oxidizing at the same time to the peroxide. Upon cooling, the brown liquid solidifies to an

* For the information contained in this section we are entirely indebted to the able and exhaustive memoir on thallium, published in the 'Journal of the Chemical Society' (Series 2, vol. ii., April, 1864), by William Crookes, F.R.S., the discoverer of this singular element.

almost black crystalline mass. The fused oxide attacks glass and porcelain, removing silica. When heated it always peroxidizes slightly. Oxide of thallium is decomposed by hydrogen at a red-heat, forming water and metallic thallium. The decomposition is however never perfect, owing to the oxide fusing and volatilizing. When fused with sulphur it forms sulphide of thallium; and in aqueous solution with metallic zinc, the metal is precipitated, and oxide of zinc formed; when an electric current is passed through a solution of the oxide, it is also reduced to the metallic state.

The best method of preparing perfectly pure hydrated oxide of thallium, is to add water to the oily compound of oxide of thallium and alcohol. This at once separates the oxide in the form of a bright yellow crystalline mass, which may be separated from alcohol and water, by exposure to warm, dry air. It is a powerful base, dissolving readily in water, and forming a colourless, strongly alkaline solution. It has a slight odour, similar to that of potassa, dissolves the skin, and feels greasy. It has a strong action on the hair and nails, staining them a deep and very permanent brown colour. It blues red litmus-paper, browns turmeric-paper, has a metallic alkaline taste, and neutralizes acids completely. It eliminates ammonia from chloride of ammonium, and reacts with hydrochloric acid, iodide of potassium, sulphide of ammonium, etc., in the characteristic manner of a thallium salt. An aqueous solution of protoxide of thallium has a greater similarity to potassa than to ammonia in its reactions with metallic salts. When added to solutions of *magnesium*, *cerium*, *manganèse*, *zinc*, *cadmium*, *lead*, *iron*, *cobalt*, *nickel*, *copper*, *mercury*, *silver*, and *peroxide of thallium*, it precipitates the respective oxides, without redissolving them in excess. From salts of *aluminum* and *chromium* it precipitates the hydrated oxides, and easily redissolves them when in excess, forming with alumina a solution unaltered by boiling, but precipitated by a current of carbonic acid, and with chromium a green solution precipitated on boiling. The salts of thallium are highly poisonous, 3 or 4 grains of the sulphate being sufficient to kill a small animal; the symptoms are somewhat similar to those produced by lead. When ignited, salts of thallium generally fuse at temperatures below redness, and then volatilize without change. On charcoal before the blow-pipe, they volatilize, communicating an intense green colour to flame.

Comportment of Salts of Protoxide of Thallium with reagents:—

Hydrosulphuric Acid produces no effect when added to a solution of sulphate or nitrate with excess of acid; if the solution be neutral, a small portion of the metal is precipitated. In solutions of oxide of thallium, combined with a weak acid such as acetic, this reagent throws down the whole of the metal in the form of a deep brown sulphide.

Sulphide of Ammonium precipitates thallium salts completely, the precipitated sulphide being insoluble in sulphide of ammonium, in caustic alkalies, their carbonates and cyanides, and only slightly soluble in acetic acid.

Hydrochloric Acid and soluble Chlorides precipitate a difficultly soluble white chloride.

Hydrobromic Acid and soluble Bromides precipitate a white, nearly insoluble bromide.

Hydriodic Acid and soluble Iodides precipitate an insoluble yellow iodide.

Alkalies, Alkaline Carbonates or Bicarbonates produce no change in thallium protosalts.

Phosphate of Soda gives a white precipitate, nearly insoluble in ammonia, easily soluble in acids.

Chromate of Potassa gives a yellow precipitate, insoluble in cold nitric or sulphuric acid, but turned orange-red on boiling in the acid solution.

Bichloride of Platinum precipitates a very pale yellow, insoluble double salt.

Phosphuretted Hydrogen precipitates a black *phosphide.*

From aqueous solutions of salts of protoxide of thallium the metal is precipitated in metallic crystals by *zinc*, and slowly by *iron.*

Peroxide of thallium (TlO_3) is always formed when metallic thallium is heated, or even when a solution of the protoxide is evaporated in the air: when the metal is burnt in oxygen the product is chiefly peroxide. It is best prepared by adding potassa, ammonia, or protoxide of thallium to a solution of the peroxide, washing the precipitate formed, and drying at a temperature of 500° F.

Anhydrous peroxide of thallium is a dark-brown powder, fusing with difficulty, and evolving oxygen at a red-heat, becoming reduced to protoxide. It is neutral to test-paper, and insoluble in water. It dissolves readily in sulphuric, nitric,

and hydrochloric acids, forming hygrometric and insoluble salts. The *hydrated* peroxide (TlO_3HO) is obtained by drying the precipitated peroxide at a temperature of 212° F.; it forms a brown powder, a shade lighter than the anhydrous oxide.

Properties of Thallium.—The most characteristic property of thallium is the intense green colour which the metal, or any of its compounds, communicates to a colourless flame. When examined in the spectroscope this colour is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line. The delicacy of the spectral reaction of this metal is so great, that Mr. Crookes was able to produce it with the five-millionth of a grain of the sulphate.

The specific gravity of thallium varies according to the treatment it has undergone. A lump, melted, and slowly cooled under cyanide of potassium, was found by Mr. Crookes to be 11·81; after being strongly compressed it became 11·88. De la Rive states it to be 11·85 after being melted, and 11·86 after being drawn into wire.

Thallium is the softest metal known, admitting of free exposure to the atmosphere. The finger-nail, or even a piece of lead, scratch it readily. It marks paper like plumbago, forming a streak, grey at first, then turning yellow, and in a day or two fading nearly out. Sulphide of ammonium or sulphuretted hydrogen will at any time temporarily restore the dark streak. Thallium has less tenacity than lead, and does not become brittle at any temperature between 0° F. and its melting-point, which Mr. Crookes places at 561° F., and M. Lamy at 554° F. It is very malleable, and can be hammered into foil as thin as tissue-paper. It can be drawn into wire only with difficulty; in this state it is almost devoid of elasticity, retaining any form into which it is bent, with scarcely a tendency to spring to its original position.

Thallium is a very crystalline metal, and crackles almost as much as tin when bent. When several pounds of the metal are fused and allowed to cool slowly, and the interior liquid portion poured off from that which has solidified, well-defined crystals, in octahedrons and fern-like forms are produced. When heated in the air, thallium begins to volatilize at a red-heat, evolving brown vapours of oxide; it boils below a white-heat, and may be distilled in a current of hydrogen: when heated to redness, and plunged into oxygen, it burns brilliantly.

The atomic weight of thallium has been found by Lamy to be 204. The results of five experiments gave Crookes 202·96, a number which he thinks may be somewhat too high. In electro-chemical position thallium is very near cadmium, being precipitated from the sulphate by zinc and iron, but not by cadmium, tin, or copper.

The position of thallium amongst the elementary bodies has given rise to considerable discussion. On the Continent it is generally classed amongst alkali metals; in England it is, on the other hand, generally regarded as belonging to the silver and lead group. Amongst the facts in favour of the relationship of thallium to the alkali metals, the following have been adduced:—It forms a readily soluble, highly alkaline oxide, a soluble and alkaline carbonate, an insoluble platino-chloride, and with alumina a double sulphate, having the crystalline form of common alum, with a similar composition. As reasons, among others, for classing thallium with the heavy metals, have been urged the complete or nearly complete insolubility of its peroxide, sulphide, phosphide, iodide, bromide, chloride, chromate and phosphate; its ready reduction from aqueous solutions of its salts by metallic zinc; the highly poisonous character of its compounds; the production of a brown insoluble peroxide by electrolytic means; its high atomic weight; the complexity of its photographic spectrum, shown by Dr. W. A. Miller to contrast strongly with the simplicity of those of the alkali metals; its low conducting power for electricity, which is close to that of lead and tin, and much inferior to that of the alkali metals; its specific heat, which coincides with that of lead; its density and melting-point, very near those of lead, and finally its physical appearance and character, which approach so nearly to those of lead, that few persons would notice at first sight any difference between the two metals.

174. Silver.

This metal is weighed as *chloride*, as *sulphide*, as *cyanide*, or in its pure *metallic* state. It is likewise estimated by volumetric processes.

Quantitative estimation as Chloride.—To the solution contained in a long-necked flask, and acidified with nitric acid, hydrochloric acid is added in excess; the whole is then well agitated, and allowed to remain for several hours in a warm place; the clear fluid is carefully separated by decantation

from the precipitated chloride, which is then washed with water acidulated with hydrochloric acid. It is then transferred to a weighed porcelain crucible, in which the washing is continued with distilled water till all traces of acid are removed. The various washings are collected in a beaker, and, if the whole be not perfectly clear, it must be allowed to stand in a warm place for several hours, and the precipitate, if any should form, must be added to the contents of the porcelain crucible. The chloride of silver, having been perfectly washed, is heated to incipient fusion, and weighed; it may afterwards be completely removed from the crucible, by reducing it by means of sulphuric acid and zinc. Should the quantity of chloride obtained in the experiment be small, it may be advisable to collect it on a filter, from which it should, after washing, be removed as completely as possible, and the filter, with the residue remaining on it, burnt, on the cover of the crucible, the ashes being mixed with the bulk of the chloride, which is then heated to incipient fusion in a counterpoised porcelain crucible as before. According to Rose, it is not admissible to precipitate silver by the *chloride of ammonium*, as this salt is capable of retaining traces of silver in solution. In cases where the presence of much chloride of ammonium is unavoidable, Gay-Lussac and Liebig recommend to evaporate the solution filtered from the chloride of silver nearly to dryness, and to treat the residue with nitric acid; on exposing the whole to heat, the alkaline chloride is converted into nitrate, while the small quantity of chloride of silver remains unaltered, and does not dissolve when the mixture is diluted.

The composition of chloride of silver is—

One equivalent of Ag . . .	108·0 . .	75·26
One ditto of Cl . . .	35·5 . .	24·74
One ditto of AgCl . .	143·5 . .	100·00

Quantitative estimation as Sulphide.—Washed sulphuretted hydrogen gas is transmitted through the solution as long as a precipitate continues to form; the whole is then warmed, and allowed to settle; it is finally collected on a weighed filter, washed as rapidly as possible out of contact of air, and dried at 212°. Silver may likewise be precipitated as sulphide from neutral and alkaline solutions by sulphide of ammonium; but, as in this case the precipitated sulphide is invariably accompanied by sulphur, it is necessary to convert it for weighing

into chloride, by digesting it with nitric acid, and then precipitating it with hydrochloric acid. Even when precipitated from acid solutions by sulphuretted hydrogen, sulphide of silver very frequently contains sulphur, from which it may be freed by digesting it with a hot, moderately strong solution of sulphite of soda.

The composition of sulphide of silver is—

One equivalent of Ag	108	87·09
One ditto of S	16	12·91
One ditto of AgS	124	100·00

Quantitative estimation as Cyanide.—Cyanide of potassium is added in sufficient quantity to redissolve the precipitate which is at first formed, dilute nitric acid is then added, and a gentle heat applied, by which the whole of the cyanide of silver is precipitated. It is washed and dried at 212°.

The composition of cyanide of silver is—

One equivalent of Cy	26	19·4
One ditto of Ag	108	80·6
One ditto of AgCy	134	100·0

Silver when combined with organic acids, is estimated in the metallic state, to which it is reduced by igniting the salt in a porcelain crucible. The heat should be gentle at first and the cover on, to prevent loss during the ignition. The lid is afterwards removed, and a strong heat applied for a considerable time, in order to effect complete combustion of the carbon of the organic acid. Silver is completely separated from all the metals of the first four groups by sulphuretted hydrogen. The solutions must in all cases be acid. Fom *lead* it may be separated by hydrochloric acid; or by heating the solution containing both metals with *cyanide of potassium*, which precipitates the lead in the state of carbonate, retaining the silver in solution as *argento-cyanide of potassium*. The silver is subsequently precipitated in the form of cyanide of silver by the addition of nitric acid.

A method of determining the amount of silver in argentiferous galena has been founded by Mène on the solubility of oxide of silver, and the insolubility of oxide of lead in caustic ammonia in excess. About 300 grains of the specimen to be analysed are pulverized, and boiled with nitric acid diluted with three or four times its volume of water in a porcelain capsule.

In a little while, all the sulphur is separated, and the lead dissolved; the filtered liquid is precipitated by a great excess of ammonia, then filtered again rapidly, and the precipitate washed with ammoniacal water. By this reagent all the oxides are precipitated at first, and afterwards those which are soluble, are again dissolved. The liquid is treated with an excess of hydrochloric acid mixed with a few drops of nitric acid to facilitate the precipitation of the silver which is separated and weighed as chloride. This process is said to be applicable in every case of analysis, whatever may be the elements contained in the specimen under examination.

Estimation of Silver in alloys (wet method).—The analysis of alloys of silver by a solution of chloride of sodium may be effected in three different ways:—1. The silver may be precipitated by an excess of the alkaline chloride, the weight of the chloride of silver produced indicating the amount of silver. 2. The quantity of chloride of sodium in a given weight of its aqueous solution being known, the amount of silver in the alloy may be ascertained by observing the weight of the alkaline chloride required to precipitate it completely. 3. The quantity of chloride of sodium in a given volume of its aqueous solution being known, the amount of silver in the alloy may be ascertained by observing the volume of the solution of alkaline chloride required to precipitate it. The last of these methods was proposed by Gay-Lussac in 1829, and as it is one of great simplicity and accuracy it is generally adopted in the British, Continental, and American mints for the assay of bars and coins of silver. The process is conducted in the following manner (Pelouze and Fremy):—

(a.) *Preparation of pure Silver*.—A certain quantity of ordinary silver is dissolved in nitric acid; should any residue remain, it is separated by decantation, the solution is diluted with water and precipitated by slight excess of chloride of sodium; the resulting chloride of silver having been well washed and dried, is reduced at a red-heat in a Hessian crucible with a mixture of chalk and charcoal, the proportions being 70·4 parts of chalk, and 4·2 parts of charcoal for every 100 parts of dry chloride of silver. The decomposition takes place in accordance with the following equation:—

$$AgCl + 2(CaO,CO_2) + C = \underbrace{CaCl, CaO}_{\text{Oxychloride of Calcium.}} + CO + 2CO_2 + Ag.$$

The reduced silver forms a button at the bottom of the cruci-

ble; it is removed, well washed, re-dissolved in nitric acid, the solution again precipitated by common salt, and the chloride again reduced by chalk and charcoal; the metal is now perfectly pure. It should be reduced to a granular state, or rolled into thin plates to facilitate its solution in nitric acid.

(b.) *Preparation of a standard or normal solution of Chloride of Sodium.*—A normal solution of chloride of sodium may be prepared by dissolving 5·414 grammes of the pure salt in 1 litre of distilled water at 15° C.; a décilitre (100 cubic centimètres) of this solution will precipitate exactly 1 *gramme* of pure silver.

It is better, however, to prepare the normal liquor from ordinary culinary salt. For this purpose 200 or 300 grammes should be dissolved in about 2 litres of water; a few grammes of the solution should be evaporated to ascertain the exact amount of salt it contains, and the solution should then be diluted with such a quantity of distilled water as would be required, supposing the salt to be pure. 1 gramme of the pure silver is dissolved in pure nitric acid, and the solution precipitated with the proper precautions by 100 cubic centimètres of the saline solution, but as the salt is not pure, this quantity will not be found sufficient to effect the complete precipitation of the silver, and it will be necessary to add a certain number of cubic centimètres of a *decinormal* saline solution, the exact composition of which is known. The volume of this solution which has been required to complete the precipitation of the silver is noted, and a calculation is made to ascertain how much of it must be added to the first solution to render it normal; the experiment should be repeated two or three times to ensure accuracy.

It is not, however, absolutely necessary that 100 cubic centimètres of the saline solution should precipitate exactly a gramme of pure silver, it suffices if it approximates very closely, and that the exact quantity of silver precipitated be known.

(c.) *Preparation of the Decinormal Saline Solution.*—100 cubic centimètres of the *normal* solution are poured into a flask of the capacity of 1 litre which is then filled up with distilled water and well mixed; it is evident that a litre, or 1000 cubic centimètres, of this solution will be required to precipitate 1 gramme of pure silver; and that one-thousandth part, or 1 cubic centimètre, will precipitate one-thousandth part of a gramme or 1 milligramme of silver.

(d.) *Preparation of the Decinormal Solution of Silver.*—One gramme of the pure metal is dissolved in 5 or 6 grammes of pure nitric acid, and the solution diluted with distilled water to exactly the volume of 1 litre. The *decinormal* silver solution and the *decinormal* saline solution are thus prepared of such strengths, that on mixing together equal volumes of each, neither nitrate of silver nor chloride of sodium remain in the liquor, but nitrate of soda is in solution, and chloride of silver precipitated in accordance with the equation—

$$AgO,NO_5 + NaCl = AgCl + NaO,NO_5.$$

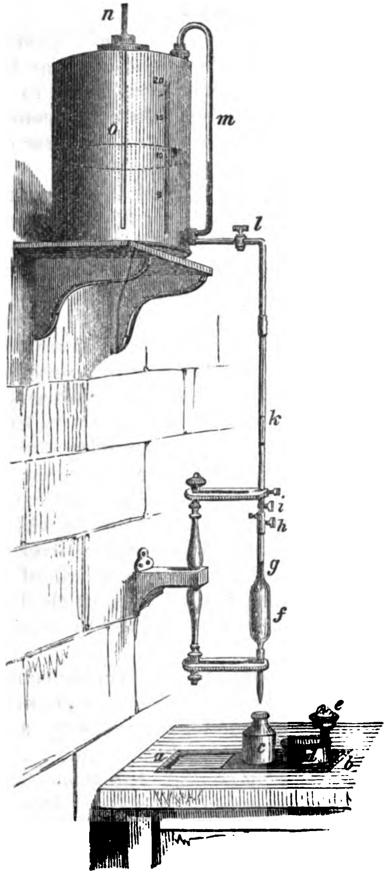


Fig. 73.

In laboratories where the wet assay of silver alloys is constantly going on, large quantities of the normal saline solution are prepared at once, and the pipette is arranged as a fixture in the manner represented in Fig. 73, where *o* represents the reservoir containing the normal saline solution, and *n* a tube through which air is admitted when the apparatus is in use. The solution is delivered from the reservoir through the bent tube *l*, furnished with a stopcock. The pipette *g f* is placed in communication with the bent delivery-tube by the tube *k* in which a thermometer is

inserted; *i* is a stopcock which serves to establish a communication between the tube *l k* and the pipette. The apparatus *a b* is employed to facilitate the exact emptying of the pipette, the tray *c d* slides backwards and forwards between two grooves, its motion in either direction being limited by the stops *a* and *b*. As seen in the figure, the assay-bottle *c* is immediately under the lower extremity of the pipette, from which the liquor can be delivered without wetting the neck or sides of the bottle; *d* is a small vessel for receiving the excess of the saline solution, and *e* is a small sponge so adjusted that when the tray is slid along the groove till it is stopped by *a*, the sponge just touches the lower extremity of the pipette. In order to fill the pipette, its lower aperture is closed by the finger, and the stopcocks *l* and *i* being opened, the solution enters from the reservoir, the air escaping through an aperture in the plug of the lower part of the stopcock, which aperture can be closed at pleasure by the plug *h*. The pipette being filled, and the aperture closed, the finger is removed, and the sponge brought in contact with its point, the plug *h* is now gently relaxed, and the liquor allowed to flow from the pipette until the mark *g* is reached, the plug is then closed, and the last drop having been removed by the sponge, the burette remains filled with exactly 100 cubic centimètres of the saline solution.

Previous to applying this process to the analysis of silver alloys, it is necessary to know approximately the value of the assay; that is, to operate upon a quantity containing nearly one gramme of silver; a tentative experiment on a gramme of the alloy with the normal saline solution will give the requisite information on this point.

Let us suppose by way of illustration that a piece of French silver coin is to be examined, which, in order to be of the standard quality as prescribed by law, should contain $\frac{897}{1000}$ths of silver. The quantity that should be taken to represent 1 gramme of silver is formed by the proportion—

$$827 : 1000 :: 1000 : x$$
$$x = 1\cdot115.$$

1·115 grm. of the alloy are therefore dissolved with the aid of a gentle heat in 5 or 6 cubic centimètres of pure nitric acid, the solution is transferred to the bottle *c*, Fig. 73, and the charge from the pipette delivered into it. The bottle is closed with its stopper, and briskly agitated for two or three minutes; if only one or two assays are being made, this may be done with

the hand, but when several samples are being operated upon, the *agitator*, Fig. 74, is employed. This consists of a frame *d* provided with a series of compartments *e e e*, etc., each of which will hold exactly one of the bottles, the frame is suspended from the steel spring *a b*, between two strong springs of vulcanized india-rubber. The stoppers of the bottles having been well secured, the apparatus is grasped by the handle *c d*, and briskly agitated for two or three minutes; the chloride of silver is soon completely precipitated, leaving the supernatant fluid quite clear. One cubic centimètre of the *decinormal* saline liquor is now delivered into the bottle from a small pipette, this pipette is a small tube open at both ends, the lower aperture being considerably contracted; it has two marks upon it corresponding to 1 and 2 cubic centimètres; it passes through the cork, and nearly to the bottom of the bottle containing the decinormal saline liquor, so that the requisite quantity can be easily withdrawn, by applying the finger to the upper end, then removing it from the bottle, and allowing the liquor to drop out from the lower aperture by relaxing the finger until the mark indicating 1 cubic centimètre has been exactly reached. Should the solution still contain silver, it is revealed by the formation of a white cloud; hereupon the bottle is again agitated, and a second cubic centimètre of the decinormal saline solution introduced. Suppose that 3 cubic centimètres have in this way been added, and that the fourth no longer produces a white cloud, the question arises, was the whole of the third cubic centimètre required or only part of it? But as this question cannot be decided, one-half of

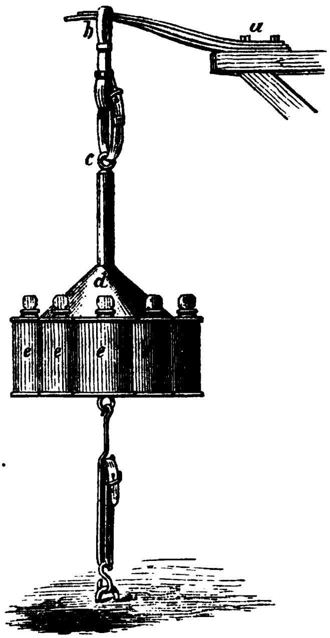


Fig. 74.

the third cubic centimètre is assumed as the real quantity; the error arising from this arbitrary measure cannot amount to more than half a millimètre, since 1 cubic centimètre of the decinormal saline liquor corresponds to 1 milligramme of silver. The result of the assay then is this:—(1) 100 cubic centimètres of the normal saline liquor, equivalent to 1·000 gr. of silver; (2) 2·5 cubic centimètres of the decinormal saline liquor, equivalent to 2·5 milligrammes of silver: the quantity of alloy submitted to analysis contains therefore 1·000 gr. + 0·0025 gr. = 1·0025 gr. of silver. The standard of the alloy is therefore found by the following proportion:—

$$1{\cdot}115 : 1000 :: 1000 : x$$

$$x = 0{\cdot}899, \text{ or the standard of the alloy is } \frac{899}{1000}.$$

Suppose, however, that *no* white cloud has arisen after the introduction of the first cubic centimètre of the decinormal solution; this shows that the whole of the silver has been precipitated by the 100 cubic centimètres of the normal saline liquor, and that quantity has probably been too much; to ascertain this, the cubic centimètre of the decinormal *saline* solution which has just been added, must be neutralized by 1 cubic centimètre of the decinormal *silver* solution, and the liquor must be agitated till clear, the operator then adds successive cubic centimètres of the decinormal silver solution, until a white cloud is no longer produced. Let us suppose that a cloud ceases to make its appearance on the addition of the fourth cubic centimètre, then, as before, one-half of the third cubic centimètre is taken as representing the real quantity that has sufficed; the 1·115 gramme of alloy contains therefore 1·0050 − 0·0025 = 0·9975 gramme of silver, and the standard is formed by the proportion—

$$1{\cdot}115 : 1000 :: 1000 : x$$

$x = 0{\cdot}8946$, which is below the legal French standard, viz. 0·897.

Dilatations and contractions are occasioned in the volume of the normal saline liquor by variations in temperature, and M. Gay-Lussac constructed a table of corrections to be applied. It is better, however, when a series of assays is about to be made, to make at the same time a standard assay with a gramme of pure silver; the exact value of the normal solution is thus ascertained, and all the assays made on the same day must be corrected in accordance with the divergence from the true value of the liquor indicated by the test experiment.

If the operator is working with English weights and mea-

sures, the solution of common salt should be made of such a strength that 1000 grain measures of it precipitate exactly 10 grains of silver, and the decimal solution of silver should be prepared by dissolving 10 grains of pure silver in nitric acid, and diluting it with distilled water till the solution occupies the bulk of 10,000 grain measures of water, each 10 grain measures of this solution will therefore contain 0·01 grain of silver.

The only metal the presence of which interferes with the accuracy of this process is *mercury*, a metal not likely to be met with in silver alloys; if present, however, it would be precipitated by the chloride of sodium together with chloride of silver in the form of *calomel*. To avoid this inconvenience, Levol recommends to supersaturate the nitric solution with caustic ammonia, then to add the test-liquor, and afterwards to supersaturate the excess of ammonia with acetic acid; he states that by this modification he is able either with the presence or absence of copper to estimate accurately silver containing a tenth part its weight of mercury. Gay-Lussac simplifies this process by adding to the nitric solution of the alloy the ammonia and acetic acid at one and the same time, but in sufficient quantity to saturate the whole of the nitric acid, both that in combination with the silver, and that in the free state. He finds acetate of soda to answer quite as well as acetate of ammonia.

Estimation of Silver in alloys (dry process).—*Cupellation:* —This method, which is the one usually adopted at Goldsmiths' Hall, and by refiners, is founded on the property possessed by silver of being unoxidizable, and nearly fixed, at a red-heat; whilst copper in the presence of lead oxidizes, and forms with the oxide of lead a fusible glass, which passes into, and is absorbed by the cupel, the silver being retained, as it were on a filter, in the form of a bright globule or button.

The *cupel*, which is best made of a mixture of finely levigated ashes of birch-wood and calcined bones, is thus prepared: the ash, slightly moistened, is laid in a brass mould somewhat deeper than that of the cupel intended to be made; in this is placed a curved and polished steel pestle, which is then struck smartly with a hammer. The operator must be careful to put as much ash into the mould as is required to make the cupel *at once*, it is otherwise apt to separate in layers when it comes to be heated. The little vessel thus made is dried with great care, and heated to redness before it is used. One

part, by weight, of the cupel absorbs during the process of cupellation the oxide formed by two parts of lead. The assayist is thus furnished with a guide to the size of the cupel required for any particular experiment.

The proportion of lead required varies with that of the copper in the alloys; it is necessary therefore before proceeding with a definite experiment to determine approximatively, the *standard* or *fineness* of the silver. In the case of a piece of coin this is generally tolerably well known, but in all cases the fineness of the silver should be ascertained by a cupellation experiment with 0·100 gr. of the alloy and 1 gr. of lead, the weight of the button obtained furnishes a sufficiently close approximation, and from this preliminary trial, the quantity of lead which should be added is ascertained by reference to the following table constructed by M. d'Arcet. The quantity of alloy usually employed is 1 gramme, the weight of the button in milligrames indicates the standard of the alloy: thus a button weighing 0 gr. 900 milligrammes represents an alloy of $\frac{900}{1000}$.

Table showing the Quantity of Lead required for the Cupellation of various Alloys of Silver and Copper.

Standard of Silver.	Amount of Copper alloyed.	Quantity of Lead necessary.	Quantity of Lead in relation to that of Copper.
1000	0	$\frac{3}{10}$	—
950	50	3	60 to 1
900	100	7	70 to 1
800	200	10	50 to 1
700	300	12	40 to 1
600	400	14	35 to 1
500	500	16 to 17	32 to 1
400	600	16 to 17	27 to 1
300	700	16 to 17	23 to 1
200	800	16 to 17	20 to 1
100	900	16 to 17	18 to 1
Pure copper	1000	16 to 17	16 to 1

Example:—Suppose a piece of silver of the approximative fineness of $\frac{900}{1000}$ is to be analysed. The quantity of lead indicated in the table, viz. 7 grammes, is placed in the cupel, which is then introduced into the muffle, and heated to bright redness in the cupel furnace. When the lead is melted, and its surface brilliant, 1 gramme of the alloy enveloped in a piece

of *pure* sheet lead is introduced into the cupel; it soon enters into fusion, and the surface of the liquid mass which is at first plane, becomes by degrees convex, in appearance it is now like a drop of oil. The fused oxide of lead is absorbed rapidly by the cupel, and a portion is volatilized and makes its escape from the muffle in the form of fumes; when the volume of the alloy is reduced to about two-thirds, the cupel is advanced to the mouth of the muffle; the surface of the button soon loses its brilliancy, and iridescent bands appear on its surface, which are occasioned by very thin layers of oxide of lead. The object of advancing the cupel to the mouth of the muffle, is to reduce the temperature of the button, which at this period becomes agitated with a rapid circular movement; this suddenly ceases, and the button having for a moment emitted a bright flash of light, technically called *fulguration* or *coruscation*, becomes white and fixed. The button should at the moment of brightening be covered with another cupel which has been kept hot for the purpose; a portion of the metal may otherwise be lost by dispersion, from *sprouting* or *spitting*. This phenomenon appears to arise from the sudden escape of the oxygen, which the silver had mechanically absorbed while in the melted state: if the button has been cooled too rapidly, a crust is formed over the surface, while the interior portion remains fluid, and upon this solidifying, the crust is ruptured by the sudden expansion of the metal, and little tubes or globules of the metal are expelled by the sudden escape of the gas. The cupel still covered, is now removed from the muffle, and when cold the globule is detached, brushed, and weighed. If the assay has been a good one, it adheres but loosely to the cupel, and its surface is clean, brilliant, and convex; but if it has been too strongly heated, it is removed with difficulty, and its surface is dull and irregular. The adherence of the button to the cupel, and the flatness of its surface, may also arise from a deficiency of lead.

In Fig. 75, A is the muffle, on each side of which is a slit *o o*; the size of this muffle is in proportion to that of the furnace, one of a convenient size should be capable of containing six or eight cupels. The muffle when introduced into the furnace is so arranged that while its closed end is supported by a shelf of refractory brick *k*, its open end corresponds exactly with the aperture *d* of the furnace, to the sides of which it is luted by a little moistened fire-clay. The fuel (charcoal or coke) is supplied through the aperture *f*, which during the operation is

closed by the door G. The interior of the muffle is in this way constantly traversed by a current of air, and the draught of the furnace is increased by the tall chimney H. The furnace having been lighted by introducing ignited charcoal by the opening, *i*, and all the apertures except that of the ash-pit having been closed, the muffle is allowed to get red-hot; the cupels which have been previously drying round the ledge of the chimney are then placed by a pair of tongs on the floor of the muffle, on which a small quantity of pounded bone-ash has been strewed, the opening *d* is now closed; the cupels are soon raised to the temperature of the muffle, and when this is the case the door is removed, and the assay dropped carefully into the cupels by a pair of light steel tongs.

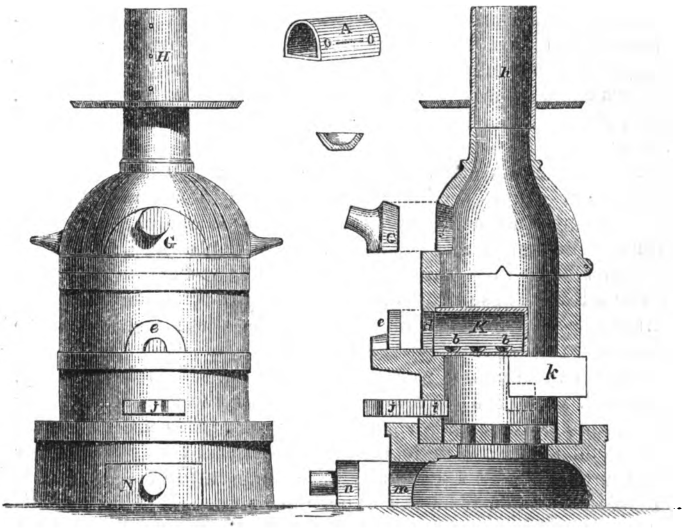


Fig. 75.

From a series of experiments made first by Tillet and confirmed and extended by D'Arcet, the following conclusions may be drawn:—

(1.) That by the process of cupellation the amount of silver is always slightly under-estimated, in consequence of a portion being volatilized and a portion being absorbed by the cupel.

(2.) That the button is not pure silver, but contains both lead and copper; a wet analysis shows that as an average, 1000 parts of the button contain four parts of foreign metals.

(3.) The more copper the alloy contains, the larger the quantity of lead required; this however is only applicable to alloys the standard of which is above 500. Copper containing a few thousandths of silver only does not require more lead than an equal weight of an alloy of 500.

Bismuth acts in cupellation in the same manner as lead, and M. Claudet has drawn up a table showing the proportions that should be used in different standards of alloys, but no application of these facts appears to have hitherto been made.

To estimate the amount of loss during the operation of cupellation, recourse is sometimes had to a "table of errors," which however cannot be made exact, because such a table implies certain invariable conditions which in practice cannot always be complied with. It is better to use with each set of assays a *check* or *proof*, that is, to make an assay with pure silver. The proof is placed in the muffle by the side of the assays; *e. g.* suppose an assay has to be made of a piece of coin the approximative standard of which is $\frac{950}{1000}$; 950 milligrammes of pure silver and 50 of copper are placed in a cupel and introduced into the muffle by the side of the alloy. Suppose that after cupellation, the proof has lost two milligrammes, this quantity must be deducted from the weight of the button furnished by the alloy. These proofs are especially useful when the alloy contains, *gold*, *platinum*, or *palladium*, as these metals tend to occasion an overweight in the button.

Some experiments were made by Mr. Hambley (Chem. Gaz., vol. xv. p. 185), to ascertain whether the loss of silver by cupellation is the same, when varying quantities are employed with a constant ratio of lead, and also to find the loss of silver when cupelled with a gradually increasing ratio of lead. The conclusions drawn from the experiments are—1. That according to the decrease in weight of the silver cupelled, so the loss of that metal very slightly increases, provided the ratio of lead employed be constant; 2. That an increasing ratio of lead produces an increasing loss of silver.

According to Field (Chem. News, vol. i. p. 277), the presence of *copper* exercises a material influence upon the loss of silver in the process of cupellation, in the estimation of that metal; when it exists as a double sulphide with copper, the loss

is very apparent, so much so indeed, that in the assay of these double sulphides, Field found it necessary to abandon the usual method and to adopt the following:—The finely powdered mineral is digested in strong nitric acid until the sulphur is yellow; the solution is somewhat largely diluted with water, and one or two drops of hydrochloric acid added. After heating gently, and allowing the supernatant liquor to become clear, it is filtered. The residue on the filter, consists of earthy insoluble matter and chloride of silver. It is dried, and the greater part mixed in a mortar with carbonate of soda, a small quantity of litharge, and a few grains of bitartrate of potassa. About half the mixture is put in a crucible, and the filter is then folded up and placed upon the powder, the remainder of which is now introduced, and the whole covered with a little fused borax. The crucible is now introduced into the furnace; an argentiferous button of lead is obtained, which is cupelled in the usual manner.

Among the various other methods of separating *silver* from *copper*, *two* may be specially noticed. *The first* consists in fusing the argentiferous copper with $2\frac{1}{2}$ parts of lead, and cooling the fused mass in thick round cakes. These cakes are then introduced into a furnace of peculiar construction, and the heat is raised sufficiently high to fuse the alloy of silver and lead, but not to fuse the copper. On cooling, the whole of the silver is found combined with the lead, from which it is separated by cupellation. *The second method* consists in dissolving the argentiferous copper in sulphuric acid, in a platinum vessel, and precipitating the silver from the solution by means of plates of copper; the precipitated copper, which is in the form of a grey metallic powder, is washed and fused with a mixture of nitre and borax; it is thus purified from the copper which may have been precipitated with it. The method has two advantages; *first*, the copper is recovered in a marketable form (that of blue vitriol); and *second*, the gold amounting to from $\frac{1}{1000}$ to $\frac{1}{1200}$th part, is saved, this metal remaining undissolved by the sulphuric acid.

To estimate the amount of silver in a compound (commercial lead for example), Pisani avails himself of the fact that iodide of starch is decolorized when poured into solutions of some salts, whilst in others it retains its blue colour. The decolorization is produced by *silver*, *mercury*, the protosalts of *tin*, *antimony*, *arsenic*, *iron*, and *manganese*, and perchloride of *gold*.

The salts of *lead* and *copper* have no action on it. In order, therefore, to estimate the amount of silver in a compound, a standard solution of iodide of starch is dropped into the solution until the last drop is undecomposed, and causes a blue tint to remain in the liquid. Instead of forming a standard solution of iodide of starch, Field dissolves iodine in iodide of potassium, and drops it into the solution of the silver salt to which a little starch-water has previously been added. The silver compound is dissolved in nitric acid, gently evaporated nearly to dryness, a slight excess of carbonate of soda introduced, and the carbonate of silver brought into solution by very weak acetic acid; a few drops of clear starch-water are added, and the ioduretted iodide of potassium dropped in from a burette. When the two liquids meet, a bright blue ring is formed, which immediately disappears on agitation, yellow iodide of silver being precipitated. When a permanent blue tinge is produced, no more silver exists in the solution. Three burettes are employed; in the first one, each division corresponds to $\frac{1}{10}$ of a grain of silver, in the second to $\frac{1}{100}$, and in the third to $\frac{1}{1000}$. When it is evident that the greater part of the silver has been precipitated by the solution from the first burette, a small quantity from the second is introduced, and the last traces are thrown down by the third. No difficulty is experienced in compounds of *silver* and *tin*, but the presence of *mercury* entirely vitiates the results, as a salt of this metal decomposes the starch compound with great facility.

175. Mercury.

This metal is in general most conveniently weighed in the metallic state. It may also be estimated in the forms of *subchloride* and *sulphide*.

Estimation as metallic Mercury:—

(1.) *Reduction in the dry way.*—The solid mercurial compound is heated in a tube of hard glass, with an excess of soda lime, precisely in the same manner and with the same precautions as are observed in the analysis of ammoniacal salts (see page 273). The open end of the combustion tube is drawn out, and bent at a somewhat obtuse angle, in order that it may be inserted into a flask containing water, into which the mercury is received; when the analysis is over, the fluid metal is collected into one large globule, by agitating the flask, it is then decanted into a porcelain capsule, and the adhering water having been

removed by blotting-paper, it is dried *in vacuo* over sulphuric acid, without the application of heat.

Rose recommends to introduce into the combustion tube, first a column of bicarbonate of soda, then one of quicklime, and then a well-blended mixture of the mercurial salt and quicklime, and finally a column of quicklime; the tube is to be heated first at the open end, finishing with the bicarbonate of soda. When the operation is ended, the bent end of the tube is cut, the mercury, collected in a flask, dried with paper and afterwards over sulphuric acid. Combinations containing iodide of mercury are not entirely decomposed when heated in this way, subiodide being condensed in the extremity of the tube simultaneously with the metallic mercury. To analyse these combinations recourse must be had to metallic copper, the operation being similar to that with quicklime.

In their experiments for determining the atomic weight of mercury, Erdmann and Marchand adopted the following somewhat complicated method of reducing the oxide, their object being the attainment of the greatest accuracy (Journ. für Praktische Chemie, xxxi. p. 385). A combustion tube about 3 feet long was drawn out in front to an open point, from 9 to 10 inches in length, and curved downwards. A loose stopper of copper shavings, which had been first oxidized by heating them while exposed to the air, and then reduced in a current of hydrogen, was introduced through the other end, and thrust forward near the point. This copper was followed by a stratum 5 to 6 inches in length, of small fragments of strongly ignited sugar-charcoal, from which every trace of dust had been carefully removed by sifting, and then the oxide (which had previously been strongly ignited in a current of air so as to remove every trace of mercurial vapour) was introduced. To advance to the front every trace of oxide which might have remained adherent to the hinder portions of the tube, it was finally rinsed with pulverulent copper: the tube, thus arranged, was treated precisely in the same manner as in organic analysis, and then placed in a long furnace. To the hinder extremities, a broad tube, filled with chloride of calcium, was fixed by means of a caoutchouc tube; to this was applied a Liebig potassa apparatus, filled with sulphuric acid, and at last a large gasometer filled with carbonic acid. The point in front of the tube was connected by a caoutchouc tube with a weighed recipient, destined to receive the mer-

cury, and in the arm proceeding from the last bulb of the latter, there was placed some gold leaf, to retain any trace of mercurial vapour which had not been condensed in the bulb. A gentle stream of the dry carbonic acid gas was first allowed to pass from the gasometer through the apparatus, the tube was then immediately surrounded with incandescent charcoal, proceeding from the front towards the hinder part, in the same manner as in an organic analysis. The carbon in the anterior portion of the tube is seen to burn at the expense of the liberated oxygen, and the mercury, which distils over in the current of carbonic acid, collects perfectly bright in the recipient. On the combustion of the charcoal, some water is formed, which passes over along with the mercury. This water is entirely removed, as well as the carbonic acid contained in the apparatus, by a current of atmospheric air at the close of the operation. By this mode of analysis these chemists obtained from four experiments the following numbers:—92·594, 92·596, 92·598, and 92·596, the mean of which, 92·596, gives as the equivalent number of mercury the figure 100·07.

A modification of this process, consisting in the employment of a current of hydrogen gas to assist in the reduction of the mercurial compound, was adopted by M. Millon (Ann. de Chim., 1846).

Hydrogen gas, he observes, is more easily obtained in a regular current than most other gases, and it greatly facilitates the decomposition of all mercurial compounds: it favours the expulsion of the water which accompanies the reduction, and likewise the condensation of the mercury in the expansion of the tube in which it is to be collected and weighed. The process is conducted as follows:—The dry gas is passed through a tube containing copper turnings heated to redness,—a plan which was found the most efficacious for preserving the perfect metallic lustre of the mercury, while it also ensured the purification of the hydrogen. On leaving the tube with the copper turnings, the gas enters the tube containing the mercurial salt. This tube should be from 14 to 16 inches long, and of the diameter of an ordinary tube for organic analysis. At a small distance from its free extremity, it is contracted, and then again contracted and drawn out at the point, and curved upwards: it thus presents a space of from 3 to 4 inches between the two contractions.

A little asbestos is first placed in the tube next the first

contracted part; then caustic lime in small fragments, to the extent of from 6 to 8 inches: the mercurial compound is next introduced, the quantity of which may vary from 15·5 to 62 grains, and then the tube is filled with caustic lime similar to the other. The tube is now placed in the furnace used for organic analysis: it receives the current of hydrogen at its wider and uncontracted extremity, and heat is applied in the usual manner. The ignited charcoal is gradually approached to the part of the tube containing the mercurial compound, and then a few pieces are placed behind it, to prevent the condensation of the metal there. The water is first seen in the portion of the tube between the contractions: it is dissipated by gently heating it. This part of the tube is then allowed to cool, and the mercury now makes its appearance, condensing in its turn without any difficulty. At the end of the operation the part of the tube containing the mercury is separated by slightly moistening the heated tube; the portion of the tube is weighed with the mercury it contains; the metal is poured out, the tube is rinsed out by nitric acid; it is then washed, dried, and weighed again. The difference between the two weights gives the weight of the mercury. The author states that by this mode of operating he has been able to drive 45 to 60 grains of mercury from one extremity of the tube to the other, condensing it between the contracted parts without the smallest loss. Two analyses of chloride of mercury yielded 73·87 and 73·82 per cent. of mercury, figures which give as the atomic weight of mercury 100·07, the same as that obtained by Erdmann and Marchand.

(2.) *Reduction in the wet way.*—The reducing agents are *protochloride of tin* and *phosphorous acid.* The process with the former is conducted as follows:—The mercurial compound, if a solid, is digested with strong hydrochloric acid; a concentrated solution of protochloride of tin, which has been rendered perfectly clear by the addition of a few drops of hydrochloric acid, is then added. The whole is boiled, but only for a few minutes, to avoid the risk of the volatilization of a portion of the mercury in company with the aqueous vapours. On cooling, the mercury is usually found deposited in the form of a black precipitate; the supernatant fluid is removed by a siphon, and the precipitate is boiled with hydrochloric acid, on which it generally loses its pulverulent appearance, and becomes converted into running globules. It is washed,

first with very dilute hydrochloric acid, and finally with distilled water; it is then received into a porcelain crucible, dried, first with bibulous paper, and lastly over sulphuric acid, in the manner already directed. When mercury has to be estimated in a liquid containing nitric acid, it is necessary to destroy this acid before a correct determination can be made: this is done by adding hydrochloric acid gradually to the solution, and concentrating by evaporation. The nitric acid is thus destroyed, free chlorine being at the same time disengaged, and the addition of the hydrochloric acid must be continued as long as the odour of chlorine is perceptible; protochloride of tin is then added, and the remainder of the operation is conducted in the manner already described. It is very difficult to obtain correct results when the solution contains much nitric acid. Whenever it is admissible, therefore, it is advisable to precipitate the mercury as sulphide, by sulphuretted hydrogen, or colourless sulphide of ammonium, having previously nearly neutralized the solution with potassa, and mixed it with excess of cyanide of potassium.

When *phosphorous acid* is employed, the mercury is precipitated as *subchloride*. When the liquid contains free hydrochloric acid, the temperature may be raised to 140° without the subchloride being reduced to the metallic state. The precipitated subchloride is not immediately formed in very weak liquids; it is necessary to leave the mixture undisturbed for twelve hours. The subchloride deposits itself readily, especially when the liquid is sufficiently acid. The precipitate is collected on a filter, washed with hot water, and dried at 212°. This process is, according to Rose, very applicable to cases where the liquid contains much nitric acid, only then the solution must be diluted with a sufficient quantity of water. Mercury can, according to the same authority, be easily separated by hydrochloric and phosphorous acids, from *copper*, *cadmium*, *zinc*, and even from *bismuth*, *antimony*, and *arsenic*. When the liquid contains bismuth, a large excess of hydrochloric acid must be added, to prevent the precipitation of oxychloride of bismuth. The mercury being separated in the state of subchloride, the bismuth is precipitated in the filtered liquid as oxychloride, then reduced to the metallic state by fusion with cyanide of potassium. If the liquid contain antimony, this metal must be retained in solution by tartaric acid, which does not hinder the precipitation of the mercurial chloride.

The composition of subchloride of mercury is—

Two equivalents	of Hg	200·0	84·92
One ditto	of Cl	35·5	15·08
One ditto	of Hg_2Cl	235·5	100·00

Estimation as Sulphide.—A stream of washed sulphuretted hydrogen is transmitted through the acid solution of the salt; in solutions of the *suboxide*, the precipitate formed is black at once; but, when a compound of *oxide* of mercury is under examination, in the beginning of the experiment white-coloured compounds of mercurial salts, with sulphide of mercury, are produced; the addition of larger quantities of the gas causes the precipitate to assume various colours, but it ends in becoming pure black. If the whole of the mercury exist in the original solution as *oxide*, it may be determined in the state of sulphide; with which view, the precipitate, occasioned by sulphuretted hydrogen, is received on a weighed filter, quickly washed with cold water, dried at 212°, and weighed; but if the mercury, or any portion of it, existed as *suboxide*, it is inadmissible to estimate it as subsulphide, because it is liable to be partly decomposed, even by a gentle heat, into sulphide of mercury and metallic mercury; and as the latter may be partly volatilized by a very gentle heat, an error of greater or less amount would be introduced (Rose). The sulphide containing a *minimum* of sulphur must therefore undergo further treatment as follows:—It is collected on a filter, and transferred, filter and all, into a wide-mouthed flask, capable of being closed by a glass stopper. A small quantity of dilute hydrochloric acid is then poured into the flask, and a slow current of chlorine conducted into the solution; the sulphide is hereby decomposed into *chloride*, *sulphuric acid*, and *free sulphur;* as soon as the latter is observed to have a clear yellow colour, the stream of chlorine is stopped, and the flask is exposed to a gentle heat to expel the free chlorine; it is then filtered off from the sulphur, and the mercury in the filtrate is estimated by protochloride of tin.

If the purity of the sulphide of mercury is questionable, Rose directs it to be redissolved and operated on as follows:—To the washed precipitate add a weak solution of caustic potassa, and pass a current of chlorine through the liquid; the sulphide is soon dissolved, especially if gently warmed; under these conditions powdered cinnabar also dissolves. The mer-

cury is entirely precipitated by sulphide of ammonium in a neutral or ammoniacal solution, without an excess of the reagent dissolving the precipitate which forms, but this is not the case when the liquid contains free potassa or soda, or the carbonates of these bases; here the alkali must be supersaturated with hydrochloric acid before precipitating the mercury. If the precipitated sulphide of mercury contain *sulphur*, it may be removed by treating it with a moderately concentrated hot solution of *sulphite* of soda, which dissolves the sulphur and becomes converted into *hyposulphite*.

The composition of sulphide of mercury is—

One equivalent of Hg	100·0 . .	86·20
One ditto of S	16 . .	13·80
One ditto of HgS . . .	116·0 . .	100·00

Separation of Oxides of Mercury from Oxide of Lead:—

(1.) *By Sulphuretted Hydrogen gas.*—The two metals are first precipitated together as sulphides from a diluted solution; the mixed sulphides are dried, and introduced into a bulb blown in a tube of hard glass, the weight of which, before and after the introduction of the sulphides, is accurately taken. The tube is connected with an apparatus for generating chlorine, and a stream of the gas, dried by passing through a tube filled with chloride of calcium, is sent through the tube. When the whole apparatus is filled with chlorine, the bulb containing the sulphides is gently heated, upon which the chloride of mercury volatilizes, and is completely separated from the chloride of lead. The sublimed chloride of mercury is driven forward by the flame of a small spirit-lamp, and received in a vessel containing water. As soon as all appearance of sublimation ceases, the tube leading from the bulb to the receiver is cut off with a file, and any crystals which may have collected in it are washed into the flask. The chloride of mercury dissolved in the receiver is precipitated by protochloride of tin, and the chloride of lead remaining in the bulb is determined by first weighing it together with the bulb, and then dissolving it out and weighing the bulb alone.

(2.) *By Cyanide of Potassium.*—This method, which is far more simple and easy of execution than the one just described, is conducted as follows:—The diluted solution of the two oxides is mixed with carbonate of soda, and then heated with excess of cyanide of potassium; the whole of the lead is precipitated

in the state of carbonate, while the mercury remains in solution in the form of double cyanide of mercury and potassium. The solution is filtered off from the insoluble lead salt, and precipitated by sulphuretted hydrogen.

(3.) *By Hydrochloric Acid.*—All the mercury present in the compound must be in the form of *oxide*. The dry mixture is treated with hydrochloric acid, and evaporated to dryness at a gentle heat. Alcohol, mixed with ether, is added to the residue, and the whole is digested: chloride of mercury alone dissolves, the insoluble chloride of lead is received on a filter, washed with alcohol, dried, and weighed. The alcoholic solution of chloride of mercury is evaporated to expel the alcohol and ether, and the mercury is then precipitated by protochloride of tin.

(4.) *By Sulphuric acid.*—Add sulphuric acid, and then alcohol forming about one-sixth of the volume of the liquid; if this does not contain sufficient hydrochloric acid, and if the proportion of sulphuric acid be insufficient, yellow subsulphate of mercury may be precipitated, which is avoided by the addition of sulphuric acid. The sulphate of lead requires washing with weak alcohol acidulated with sulphuric acid.

Separation of Oxide of Mercury from Oxide of Silver:—

(1.) *By Hydrochloric acid.*—Add a sufficient quantity of hydrochloric acid to the diluted solution; after the deposition of chloride of silver, decant the supernatant liquid, then heat the chloride precipitate with a small quantity of nitric acid, add some water, and a few drops of hydrochloric acid, and then filter. Precipitate the mercury from the filtered liquid by phosphorous acid (Rose).

(2.) *By Cyanide of Potassium.*—The solution is nearly neutralized with potassa; excess of cyanide of potassium is then added, by which the precipitate which first forms is entirely redissolved, and the solution contains the double cyanides of silver and potassium, and of mercury and potassium. On adding nitric acid, the cyanide of potassium is decomposed, the silver is precipitated in the form of cyanide of silver, while the cyanide of mercury remains in solution; the former is separated by filtration, and from the filtrate, the mercury is precipitated by sulphuretted hydrogen.

(3.) *By Chlorine.*—This is effected precisely in the same manner and with the same apparatus as is employed in the separation of oxide of mercury from *oxide of lead;* chloride of silver remains in the bulb, in which it is weighed, the bent tube,

through which the volatilized chloride of mercury makes its escape into the receiver having been cut off. The fused chloride of silver must, after weighing, be removed from the bulb by zinc and sulphuric acid, in order that the weight of the latter may be taken.

Separation of Suboxide of Mercury from Oxide of Mercury.—The solution is diluted considerably with water, and the suboxide is precipitated as subchloride by hydrochloric acid: heat must be avoided. The subchloride, after standing for some time, is received on a weighed filter, and dried at a gentle heat. The oxide of mercury in the filtrate is precipitated by protochloride of tin. If the substance be a solid and insoluble, it is acted upon at a low temperature, with diluted nitric acid, until it is completely dissolved; hydrochloric acid is then added as before.

Analysis of amalgams.—If the metal or metals with which the mercury is combined are not volatile, or oxidizable by heat with access of air, the amount of mercury in the amalgam may be ascertained in the simplest manner by igniting it in a porcelain crucible. If, however, the metals are liable to alteration by exposure to heat in an open vessel, the ignition must be performed in a retort, the neck of which, after the volatilization of the mercury, must be closed up by the blowpipe, while the retort is still ignited.

176. Bismuth.

This metal is almost invariably weighed as *oxide;* it is precipitated from its solution in nitric acid by carbonate of ammonia; the solution should be diluted, and it should be heated nearly to boiling for a few minutes before it is filtered, otherwise a portion of the oxide will be retained in solution by the precipitant. Neither carbonate of potassa nor carbonate of soda can be substituted for carbonate of ammonia; a portion of the former is carried down with the precipitate, and is not easily removed by subsequent washing, and the latter fails to effect a perfect precipitation. The carbonate of bismuth, having been washed, is separated from the filter, and ignited in a porcelain crucible, by which it loses carbonic acid, and becomes converted into protoxide of a yellow colour. The filter is burnt on the cover of the crucible, and its ashes added to the oxide.

The composition of teroxide of bismuth is—

One equivalent of Bi	210 . .	89·74
Three ditto of O	24 . .	10·26
One ditto of BiO_3 . . .	234 . .	100·00

In the presence of sulphuric or hydrochloric acids, bismuth cannot be effectually precipitated by carbonate of ammonia, as in the former case a basic sulphate, and in the latter a basic chloride, is at the same time precipitated, and neither of these salts can be subsequently decomposed even by protracted digestion with excess of carbonate of ammonia. In such cases it is necessary, in the first place, to mix the solution of the bismuth salt with acetic acid (water will not do, as it would cause the formation of an insoluble basic salt), and then to precipitate the bismuth in the form of sulphide by sulphuretted hydrogen, or by sulphide of ammonium, having previously rendered the solution alkaline by the addition of caustic ammonia. The precipitated sulphide, having been washed, is decomposed by digesting it, filter and all, with nitric acid; the solution is diluted with weak acetic acid, filtered, the filter washed with the same diluted acid, and the filtrate finally precipitated by carbonate of ammonia.

Separation of Oxide of Bismuth from Oxides of Lead:—

(1.) *By Sulphuric Acid.*—An excess of sulphuric acid is added to the solution containing the two oxides, and heat is applied till the sulphuric acid begins to volatilize: it is then quickly filtered, and the sulphate of lead is washed with water acidulated with sulphuric acid. The sulphate of bismuth in the filtrate is precipitated by carbonate of ammonia. The results are not very accurate, since sulphate of lead is not altogether insoluble even in dilute sulphuric acid. A better plan is the following:—The solution of the two oxides in nitric acid is evaporated to dryness in a porcelain capsule on the water-bath: the dry residue is taken up by distilled water, and again evaporated, when all free nitric acid is expelled, and the residue of bismuth is completely converted into a basic salt; the capsule is allowed to cool with its contents, which are then treated with a cold aqueous solution of nitrate of ammonia of known strength. The solution is left for some time in contact with the solid residue, in order that the soluble nitrate of lead may be completely taken up by it. The solution of nitrate of lead is filtered off, and the insoluble basic nitrate of bismuth which remains, is washed with the solution of nitrate of ammonia. The oxide of lead may be precipitated as sulphate. The washing must not be continued too long. (Löwe.)

(2.) *Ullgren's process.*—The two oxides are together precipitated with carbonate of ammonia, and redissolved in acetic

acid. A strip of *clean lead*, of known weight, is then put into the solution, so that the whole of it is covered. The vessel is closed, and allowed to stand for some hours. The bismuth is separated in the metallic state, and that which remains on the strip of lead is washed off, and the strip dried and weighed. It is brought on to a filter, and washed with water that has been boiled and allowed to cool; it is then dissolved in nitric acid, evaporated to dryness, ignited, and the oxide weighed. The solution of lead is precipitated with carbonate of ammonia, and the weight of the oxide determined from this, is to be deducted, the oxide corresponding to the loss which the strip of lead has suffered during the operation.

(3.) *By Heat.*—The process is the same as that employed for the separation of *silver* from *mercury*, and *lead* from *mercury*, namely, by converting the metals into chlorides by heating them in an atmosphere of chlorine, and expelling the volatile chloride of bismuth by heat. Too high a temperature must be avoided, otherwise a portion of the chloride of lead may be also volatilized. The proportion of bismuth may be calculated from the loss of weight which the compound under examination experiences.

(4.) *Liebig's method.*—To a cold solution of the nitrates of the two oxides *carbonate of lime* is added, which precipitates the bismuth, but not the lead.

(5.) *By Caustic Potassa.*—To the nitric solution caustic potassa is added; both oxides are precipitated; but on adding excess of the caustic alkali the oxide of lead is redissolved.

Separation of Oxide of Bismuth from Oxide of Silver :—

(1.) *By Hydrochloric Acid.*—Nitric acid is added to the solution, and then hydrochloric acid, which precipitates the silver as chloride. The bismuth in the filtrate is precipitated by sulphuretted hydrogen, the sulphide decomposed by nitric acid, and finally precipitated by carbonate of ammonia.

(2.) *By Cyanide of Potassium.*—This reagent is added to the solution of the two oxides, whereupon the bismuth is precipitated as carbonate; the silver remains in solution as double cyanide of silver and potassium; it is separated by filtration from the carbonate of bismuth.

177. Cadmium.

This metal may be quantitatively estimated as *oxide* or as *sulphide*.

Estimation as Oxide.—The solution under examination is precipitated by carbonate of potassa, and the resulting white carbonate of cadmium is decomposed by ignition into carbonic acid and water, which escape, and oxide of cadmium, which remains behind in the form of a brown powder. Ammoniacal salts interfere with the complete precipitation of oxide of cadmium by alkaline carbonates; carbonate of ammonia cannot, therefore, be employed as the precipitant. In precipitating oxide of cadmium by carbonate of potassa in the presence of ammoniacal salts, the same precautions must be taken as in the precipitation of carbonate of zinc under similar circumstances.

The composition of oxide of cadmium is—

One equivalent of Cd	56	87·5
One ditto of O	8	12·5
One ditto of Cd O	64	100·0

Precipitation as Sulphide.—This may be effected either by sulphuretted hydrogen or by sulphide of ammonium; in acid solutions the former reagent is employed. It should be largely diluted, and the gas allowed to pass slowly through the liquid for a long time; the resulting sulphide is of a yellow or orange colour, according as the solution has been more or less diluted. It is collected on a weighed filter, washed with distilled water, and dried at 212°.

The composition of sulphide of cadmium is—

One equivalent of Cd	56	77·78
One ditto of S	16	22·22
One ditto of Cd S	72	100·00

When sulphide of ammonium is employed as the precipitant, the sulphide of cadmium should be decomposed by digestion with hydrochloric acid, and the solution precipitated with carbonate of potassa. It has been observed by Dr. Reinsch (Jahrb. für Prakt. Phar., xiii. p. 72) that when a salt of cadmium is dissolved in hydrochloric acid, and then treated with sulphuretted hydrogen, no precipitate takes place till after the gas has been passed through the solution for a long time, and that then the precipitate is a combination of sulphide of cadmium with chloride. On edulcorating with water, the chloride is dissolved, and the yellow sulphide is left on the filter. This observation shows the necessity of diluting the solution before passing the

gas through it. He has observed, also, that in precipitating a hydrochloric solution containing copper, lead, bismuth, and cadmium by sulphuretted hydrogen, the three former metals are completely thrown down before the chloride of cadmium is at all decomposed; the filtered liquor gives no traces of either of the three first metals, but on continuing to pass the gas slowly through it for a long time, the cadmium is precipitated of its characteristic yellow colour.

Separation of Oxide of Cadmium from Oxides of Lead:—

(1.) *By Cyanide of Potassium.*—The diluted solution of the oxides is first rendered slightly alkaline by carbonate of soda; cyanide of potassium is then added, and heat applied. The lead is precipitated as carbonate, the cadmium remains in solution as double cyanide of cadmium and potassium, and may be precipitated from the filtered solution by sulphuretted hydrogen.

(2.) *By Sulphuric Acid.*—The solution is concentrated, and excess of dilute sulphuric acid added; sulphate of lead precipitates, which is received on a filter and washed, first with dilute sulphuric acid, and finally with alcohol; the cadmium in the filtrate is precipitated by carbonate of potassa; the former method with cyanide of potassium gives the best results, in consequence of the partial solubility of sulphate of lead, even in dilute sulphuric acid.

Separation of Oxide of Cadmium from Oxide of Silver:—

(1). *By Hydrochloric Acid.*—To the diluted solution, nitric acid is added, and then slight excess of hydrochloric acid, the liquor filtered from the precipitated chloride of silver contains the cadmium, which is precipitated by carbonate of potassa.

(2.) *By Cyanide of Potassium.*—The nitric solution of the two metals is rendered neutral by the addition of potassa; cyanide of potassium is then added in such quantity that the precipitate, which is at first formed, is entirely redissolved. To the clear solution, excess of nitric acid is next added, whereupon the whole of the silver is precipitated as cyanide: the cadmium remains in solution, and may either be precipitated by sulphide of ammonium, the liquid having been previously rendered slightly alkaline by the addition of potassa; or the hydrocyanic acid may be expelled by evaporating with sulphuric acid, and the cadmium precipitated as carbonate by carbonte of potassa.

Separation of Oxide of Cadmium from Oxide of Mercury.—

This may be effected by *formiate of soda*, but the process is tedious, and requires considerable care. Hydrochloric acid is added to the solution, which is then nearly saturated with potassa; excess of formiate of soda is then added, and the solution is set aside for some days at a temperature not above 170°. The mercury precipitates in the form of calomel; the solution filtered from the subchloride of mercury contains the cadmium, which is then precipitated by carbonate of potassa. Cyanide of potassium may also be employed to separate these two oxides in the following manner:—The clear solution is rendered neutral by potassa, and excess of cyanide of potassium is then added. To the solution of the two cyanides very dilute nitric acid is added, and the whole is boiled; the mercury salt is not decomposed: the cyanide of cadmium, on the other hand, is converted into nitrate, and may, consequently, be decomposed by carbonate of potassa: the filtrate, from the carbonate of cadmium, containing the oxide of mercury, may be precipitated by sulphuretted hydrogen.

Separation of Oxide of Cadmium from Oxide of Bismuth.—This likewise is effected by cyanide of potassium; an excess of the cyanide is added, and heat applied, the whole of the bismuth is separated as carbonate, and the cadmium is precipitated either by sulphuretted hydrogen or by carbonate of potassa, the solution filtered from the carbonate of bismuth, having been previously boiled with hydrochloric acid. Advantage may also be taken of the insolubility of chromate of bismuth, and the solubility of chromate of cadmium, to effect a separation of these two metals.

Separation of Oxide of Cadmium from Oxide of Zinc (Aubel and Ramdohr).—To the solution of the two oxides tartaric acid is added, and then solution of soda; it is then largely diluted and boiled for two hours, the oxide of cadmium is completely precipitated, the oxide of zinc remaining in solution, from which, after filtering off the oxide of cadmium, it is precipitated by sulphuretted hydrogen. The sulphide of zinc is redissolved in hydrochloric acid, the solution poured into a boiling solution of carbonate of soda, and the basic carbonate of zinc thus obtained, is converted into oxide by calcination.

178. Copper.

There are various methods of estimating this important metal. It may be weighed as *oxide*, as *sulphide*, as *subiodide*,

and in the ***metallic state;*** it may also be determined by various volumetric processes.

(1.) *Determination as Oxide.*—If the salt to be examined be soluble in water, or in nitric acid, provided no organic substance be present, it is best precipitated by ***caustic potassa.*** The solution is considerably diluted, and raised to the boiling temperature in a capacious porcelain basin, and the caustic alkali gradually added as long as a brownish-black precipitate is produced; the boiling is continued for a few minutes, and the precipitated oxide is then received on a filter, and washed with boiling water. The greater part of it is then removed from the filter, and transferred to a platinum crucible, in which it is ignited. The filter, with its adhering oxide, is dried, burnt on the cover of the crucible, and the ashes added to the main bulk of the oxide. As oxide of copper absorbs moisture rapidly from the atmosphere, it must be weighed as soon as it is sufficiently cold to be placed in the scale of the balance, and it is advisable to allow the crucible to cool underneath a receiver by the side of a vessel containing concentrated sulphuric acid. If the solution be not dilute, the precipitation by caustic potassa is incomplete, as is rendered evident by the filtrate becoming discoloured when mixed with sulphuretted-hydrogen water, the same is the case if any organic matter be present; in either of these cases, the filtrate must be concentrated by evaporation, precipitated by sulphuretted hydrogen, and the precipitate treated as will be presently described. The oxide on the filter must be well washed with boiling water, to remove all traces of the alkali, which is invariably carried down in company with the oxide, during its precipitation.

The composition of oxide of copper is—

One equivalent of Cu . . .	31·75	. . 79·87
One ditto of O . . .	8	. . 20·13
One ditto of CuO . . .	39·75	. . 100·00

(2.) *Precipitation and estimation as Sulphide.*—The solution is acidified with hydrochloric acid, diluted with water, and a stream of washed sulphuretted hydrogen gas passed through it till it is perfectly saturated. The precipitated sulphide is received on a filter, and washed as quickly as possible with water impregnated with sulphuretted hydrogen; it is removed as completely as possible from the filter, which is then dried and ignited, and its ashes mixed with the bulk of the precipitate. The sul-

phide is decomposed by digestion with dilute nitro-hydrochloric acid, and, the sulphur being separated, the solution is evaporated with sulphuric acid, until the nitric acid is entirely expelled; a large quantity of water is then added, and the oxide is precipitated by caustic potassa at the boiling temperature. If the solution be neutral or alkaline, sulphide of ammonium may be employed as the precipitating agent.

According to Rose, copper may be quantitatively estimated as sulphide, by calcining the precipitate by sulphuretted hydrogen in a current of hydrogen. The operation is performed in a crucible, through which a stream of dry hydrogen is made to pass. The heat must not be applied until the whole apparatus is full of hydrogen, and it is indispensable to continue the disengagement of gas until the crucible is quite cold.

(3.) *Estimation as Subiodide* (Pisani).—To the solution previously freed from all metals whose iodides are insoluble, sulphurous acid is added; then, after having applied a gentle heat, iodide of potassium until the supernatant liquor has lost the colour due to the presence of copper, and the formation of a precipitate ceases. The subiodide of copper being very dense, settles readily, especially when heated, like chloride of silver. In this precipitation, the sulphurous acid must always be in a slight excess to avoid the formation of the brown compound. After having heated the liquor nearly to boiling, it is filtered on a counterpoised filter; the precipitate is washed with hot water and dried; it is heated with the filter to from 230° to 248° F., after which the subiodide is weighed, and from its weight the quantity of metal is calculated.

The composition of subiodide of copper is—

Two equivalents of Cu . . .	63·5 . .	33·33
One ditto of I . . .	127·0 . .	66·67
One ditto of Cu_2I . .	190·5 . .	100·00

(4.) *Estimation as metallic Copper in ores.* (F. Mohr, 'Répertoire de Chimie pure et appliquée,' and Chem. News, Nov. 8th, 1862.)

(a.) *Oxygenated ores*, comprising *Oxide, Suboxide, Malachite*, and *Phosphate of Copper*.—According to the richness of the ore to be assayed, from 75 to 150 grains of the mineral reduced to an impalpable powder, are heated with weak sulphuric and nitric acids. The mixture is boiled, evaporated to dryness, and then calcined until it ceases to disengage vapours. The copper be-

comes transformed into sulphate, not decomposable by moderate heat, and very soluble in sulphuric acid. On the contrary, iron is converted into slightly soluble ferric subsulphate, and lead into insoluble sulphate. With *tin* and *antimony*, nitric acid forms oxides which resist the action of solvents. When the capsule is cool, distilled water is added and the solution boiled. It is then filtered, the filtrate contains all the copper, and small quantities of ferric sulphate. On treating this solution with *zinc*, the ferric salt is reduced, and the copper precipitated by boiling, in the metallic state. To make sure of the complete precipitation of the metal, it suffices to add a little solution of sulphuretted hydrogen to a drop of the supernatant liquid. To free the copper from excess of zinc, the powder is treated with hydrochloric acid, until it ceases to disengage bubbles of hydrogen gas. The metal freed from zinc is washed with hot distilled water; the action of the air must be avoided when the solution is acid, because a portion of copper would dissolve; but it is easy to avoid this inconvenience by effecting the washing promptly. The reduced copper is dried in the water oven till it ceases to lose weight. The presence in the ore, of *zinc*, *manganese*, *iron*, *cobalt*, and *nickel* does not affect the precision of the analysis, neither of these metals being precipitated by zinc.

(b.) *Sulphuretted ores.*—The treatment by sulphuric and nitric acid must be several times repeated, drying and calcining the metal between each treatment with acid. This method, the author thinks, has the advantage of being applicable to all ores, whatever their composition, and of not necessitating a preliminary qualitative analysis. In the second place, the copper is separated from metals (*lead*, *tin*, and *antimony*), from which it is freed with difficulty by ordinary methods, whilst four metals (*zinc*, *iron*, *cobalt*, *nickel*) do not influence the exactness of the estimation, and may be disregarded.

Lovel's method of determining Copper.—This is a modification of the method proposed by Fuch for the quantitative estimation of iron (see page 313). The cuprous solution is introduced into a flask that can be accurately closed with a glass stopper, ammonia is added, till the liquid assumes a transparent blue colour, and the flask is then filled with water, from which all atmospheric air has been expelled by boiling; a clean and accurately weighed slip of copper is introduced into the bottle, which is immediately closed; when the liquor has become per-

fectly colourless, the slip is removed, washed, dried and weighed, the diminution in weight which it has undergone, indicates the amount of copper originally present in the solution. The result which, when properly conducted, is very accurate, depends on the abstraction of one equivalent of copper from the slip by every equivalent of oxide of copper in the solution to form an equivalent of suboxide of copper, which forms with ammonia a colourless solution, thus:—

$$CuO + Cu = Cu_2O.$$

It requires a considerable time to complete the process, which is obviously altogether inapplicable in the presence of foreign metals, which are capable of being precipitated by copper.

Cassaseca's method.—This consists in dissolving the copper compound in an acid, adding an excess of ammonia to the solution, and comparing the tint furnished by this solution, with that which a known weight of pure copper yields likewise in the state of ammoniuret.

(5.) *Volumetric methods of estimating Copper:*—

(a.) *Pelouze's method* ('Comptes Rendus,' Feb. 12, 1846).—This mode of analysis was suggested to the author, by the accuracy and rapidity with which alloys of silver are analysed by the process discovered by M. Gay-Lussac. He succeeded in effecting his object in several different ways, all based principally on the phenomena of precipitation, and simultaneous decoloration. The following was the mode of proceeding which he finally adopted:—a certain quantity of very pure copper is dissolved in nitric acid, the solution is diluted with water, and excess of ammonia added; a deep blue solution is obtained. On the other hand, some sulphide of sodium is dissolved in water, and poured into a tube graduated and divided into tenths of a cubic centimètre; the ammoniacal solution is heated to boiling, and the solution of the sulphide gradually added. If we suppose that it required 31 cubic centimètres to decolorize 1 gramme of copper, we have a standard solution of known strength. To apply this to the analysis of copper alloys, a certain known weight is dissolved in aqua-regia, the solution is supersaturated with ammonia, heated to boiling, and the standard solution of the sulphide added until it is decolorized, taking care to add from time to time, a little dilute ammonia to replace that which is evaporated. The decrease in the depths of the blue tint, points out that the end of the experiment is more or less near, and when it is requisite to add the last portions of the sulphide in drops. When

the operation is supposed to be finished, the number of divisions employed for the decoloration is read off, and compared with the number required to decolorize an equal weight of pure copper. It must be remarked that the ammoniacal liquor from which the copper has been precipitated does not long remain colourless, but gradually becomes blue in consequence of the sulphide of copper becoming partially converted into sulphate by the absorption of oxygen. This mode of operating is not, according to the author, liable to an error amounting to more than $\frac{5}{1000}$ or $\frac{6}{1000}$, though still greater accuracy is obtained by completing the decoloration of the blue liquid with a very weak solution of sulphide, precisely in the manner recommended by Gay-Lussac in his 'Analysis of Silver Alloys by Standard Solutions of Common Salt.' Neither *tin*, *zinc*, *cadmium*, *lead*, *antimony*, *iron*, *arsenic*, nor *bismuth* in any way interfere with the success of this process, not being in the least affected by the sulphide of sodium while a trace of copper remains to be precipitated; indeed the author found that when the sulphides of zinc, cadmium, tin, lead, bismuth, and antimony are placed in contact with ammoniacal solution of sulphate of copper, they decolorize it, some in the cold, others with the assistance of heat, which proves very evidently, that these sulphides cannot exist, except perhaps for an instant, in a solution of copper. Their formation subsequently to the decoloration, has no influence on the result of the analysis, as the termination of this is judged of by the decoloration of the liquid, without paying the least attention to the precipitates which subsequently form; or, if any attention *is* paid, it is only with a view to obtain some knowledge of the nature of the metals which accompany the copper. Thus, if any alloy consists of copper, lead, tin, and zinc, the presence of *zinc* is readily detected by the white precipitate which succeeds the black precipitate of sulphide of copper, the lead and tin being precipitated at the outset by ammonia. *Cadmium*, like zinc, is precipitated immmediately after the copper. The very moment the liquid is observed to be decolorized, a beautiful pure yellow precipitate of sulphide of cadmium is formed, if the addition of sulphide be continued. If the alloy contain *silver*, that metal is previously precipitated from the nitric solution by hydrochloric acid. In this method of estimating copper, an important property of ammonia, besides that of heightening the colour, is that it prevents the salts of copper being precipitated by *sulphites* and *hyposul-*

phites, without which it would probably have been impossible to estimate the copper by means of solutions of the alkaline sulphides, since these salts almost always occur in the alkaline sulphide, and are moreover produced from them by contact with the air. A solution of sulphide of sodium becomes weaker by contact with the air, but the alteration is very slow, nor is it necessary to change the liquid as long as any remains in the flask in which a quantity has been prepared. The only precaution to be taken, and it is one which applies to all standard solutions, is to determine previously to each assay, the actual strength of the *sulphide* with a known weight of pure copper. Pelouze states in conclusion, that this method, applied to the analysis of copper ores, yields results of the greatest accuracy.

(b.) C. Mohr's *method* (Liebig's 'Annalen,' xcii. p. 97).—This is founded on the fact that salts of protoxide of copper are precipitated by metallic iron, the latter being converted into protoxide. The quantity of the protosalt of iron is determined by permanganate of potash.

The solution of the copper salt is put with a few drops of hydrochloric acid, and about one-fourth of pure chloride of sodium, into a stoppered bottle; a quantity of soft iron wire is then introduced. The reduction immediately commences, and should be assisted by a heat of from 89° to 100° F. All the copper is separated in a metallic form in an hour or two, when no trace of copper can be detected in the solution by sulphuretted hydrogen. The following precautions must be observed; —the solution must not be too acid, as in that case an excess of iron is dissolved; and the heat applied must not be too strong, as this causes the separation of a basic protosalt of iron in the form of a flocculent precipitate, which has no action upon the permanganate of potassa; when the reduction is completed, which may be known by the clearness of the fluid, a protosalt of iron has taken the place of the protosalt of copper, according to the formula—

$$CuO + SO_3 + Fe = FeO + SO_3 + Cu.$$

The fluid with the separated pulverulent copper is then diluted, and a measured quantity drawn off by a pipette and treated with permanganate of potassa.

(c.) Schwartz's *method* (Annal. der Chemie und Pharm. 84). —This is based on the fact that suboxide of copper reduces iron from the state of sesquichloride to that of protochloride, thus:—

$$Cu_2O + Fe_2Cl_3 + HCl = 2\,CuCl + 2\,FeCl + HO.$$

To a solution of the compound in nitric acid, or in water contained in a porcelain basin, is added a solution of neutral tartrate of potassa, and then potassa or soda in excess; the blue fluid obtained, is warmed on the water-bath with an aqueous solution of grape or milk sugar; the action is allowed to continue until the blue fluid begins to turn brown, the precipitate, consisting of suboxide of copper, is allowed to subside, and then filtered and washed with hot water, till the washing water passes through colourless. The filter with its contents are then transferred to the porcelain basin, and *pure* sesquichloride of iron added in slight excess, together with a little hydrochloric acid, gentle heat is applied, and when the subchloride of copper which is at first formed is redissolved, the solution is filtered into a capacious flask, and the remains on the filter well washed; it is then allowed to cool to about 77°, and the amount of protochloride of iron determined by a standard solution of permanganate of potassa. Every 28 parts of iron found in the state of protochloride, indicate 31·75 parts of copper.

(d.) *Fleitmann's method* (Liebig's 'Annalen,' April, 1856, p. 141).—When the solution of copper is free from nitric acid, or injurious metals, such as antimony and arsenic, the copper is precipitated with pure *metallic zinc*, the excess of which metal is got rid of by digestion with pure sulphuric acid; the precipitate is washed, and dissolved in an acid solution of pure perchloride of iron. The solution of the copper takes place almost instantaneously, and furnishes double its equivalent of protoxide of iron, which is determined by permanganate of potassa; when nitric acid is present, ammonia is added in excess, and the precipitation of the copper effected in the filtered solution, by pure zinc shavings.

(e.) *Terreil's method* ('Comptes Rendus,' Feb. 1, 1858).—The cuprous mineral is dissolved in nitric acid, which is completely driven off by concentrated sulphuric acid, the nitrates being converted into sulphates, ammonia is added in excess, and the liquid filtered; it is then boiled with sulphite of ammonia until colourless, and the excess of sulphurous acid is driven off by boiling with hydrochloric acid, the solution is then diluted with water, and treated with a standard solution of permanganate of potassa.

(f.) *By Cyanide of Potassium* (Parker and Mohr).—The substance is dissolved in an acid, and ammonia added in excess; a normal solution of cyanide of potassium is then added from a

burette until the blue colour disappears; *two* equivalents of cyanogen are necessary to decolorize one of copper in ammonia. In this method Field, who has subjected the various processes for determining copper to a critical examination (Chem. News, vol. i. pp. 24, 61, 73), remarks that great caution and considerable practice are required to determine the necessary amount of cyanide, as towards the end of the process, the decolorization is not very distinct, the solution assuming a delicate violet tint which fades very gradually, leaving at length the liquid destitute of colour; it is safer to leave a very slight tint, as it disappears after the lapse of twenty-four hours. If iron be present, it is better not to filter off the peroxide precipitated by ammonia, as it is exceedingly difficult to wash the copper out of it, and the estimation of the copper can be perfectly effected in the solution, in its presence. The solution of cyanide recommended by Field is 1300 grains of the salt dissolved in four pints of water, about 50 grains of the mineral being employed; with alloys of *tin* and *copper*, *antimony* and *copper*, and *arsenic* and *copper*, this method is available; but it cannot be applied to the analysis of alloys of *copper* and *zinc*, or of *copper* and *silver;* the presence of *nickel* and *cobalt* likewise interferes with its accuracy. Fleck (Polytech. Centralblatt, 1859, p. 1313) recommends to dissolve the copper compound in *carbonate of ammonia* instead of ammonia, and to add a drop of ferrocyanide of potassium to the blue liquor. The moment the cuproammoniacal compound is destroyed, the liquid becomes *red.*

With regard to the precipitation of copper by iron or zinc, Field remarks that though the estimation is never *perfectly* correct, traces both of zinc and iron being found with the precipitated copper, however carefully the operation is performed, nevertheless in a commercial point of view it is not far from the truth; but the precipitated copper should be washed with water at the temperature of 100° or 120°, to which one or two per cent. of hydrochloric acid has been added; if a stronger acid be used there is a danger of some of the finely precipitated copper being dissolved.

(g.) *Streng's method.*—The oxide of copper is reduced by grape sugar, a solution of starch and iodide of potassium added, afterwards a standard solution of bichromate of potassa; the following reaction occurs:—

$$3\,Cu_2O + 2\,CrO_3 = 6\,CuO + Cr_2O_3.$$

When the whole of the subchloride of copper is converted

into chloride, a permanent blue colour is produced; the chromic acid then reacting on the iodide of potassium and expelling iodine. Field finds this method to give accurate results, provided care be taken in the addition of the iodide of potassium. Diniodide of copper is very insoluble in hydrochloric acid, unless the latter be in excess, so that when a considerable quantity of alkaline iodide is employed, and little hydrochloric acid present, there is not much dichloride of copper in solution.

MM. Plessy and Moreau have founded a method of estimating copper on the following reaction:—

$$CuCl + Cu = Cu_2Cl.$$

The solution of protochloride is made as nearly neutral as possible by the addition of ammonia, and the liquor is then rendered green by the cautious addition of hydrochloric acid: a strip of copper is boiled in this solution until it becomes colourless; the loss of weight indicates the amount of metal in the chloride.

E. O. Brown (Quart. Journ. Chem. Soc. vol. x. p. 65) dissolves the copper compound in nitric acid, adds carbonate of soda, and afterwards acetic acid in excess. Iodide of potassium is then added, equal to at least six times the weight of the copper. A standard solution of hyposulphite of soda is poured into the flask from a burette, until the brown colour nearly disappears. Clear starch liquid is then introduced, and a further addition of hyposulphite, until the blue colour is destroyed. The presence of peroxide of iron is fatal to this method, not only on account of the deep colour of the peracetate of iron, but more particularly because the peroxide becomes partially deoxidized by the hyposulphite, and thus interferes with the reaction.

In concluding his valuable review of the various methods of estimating copper, Field remarks that much must be left to the knowledge and experience of the operator. In a mixture of *lead*, *arsenic*, and *copper*, the cyanide of potassium process could be advantageously adopted, whilst the method by precipitation would be worthless, as all the metals would be reduced. Manganese and zinc do not, on the other hand, affect the precipitation of copper upon iron, but render the cyanide estimation valueless.

Kunsel has recently proposed the following modification of Pelouze's volumetric method for the estimation of copper:—*Sulphide of zinc* is employed for indicating the complete pre-

cipitation of the copper, that substance being instantly decomposed in a hot ammoniacal solution of copper. The solution of sulphide of sodium is of such a strength that one cubic centimètre precipitates a centigramme of copper. The sulphide of zinc is prepared by dissolving the metal in hydrochloric acid, supersaturating with ammonia, and then boiling with a little sulphide of zinc to remove the *lead*, which is always present in commercial zinc. The ammoniacal solution of zinc is filtered and decomposed with sulphide of sodium, a small quantity of zinc being allowed to remain in solution. The moist sulphide of zinc, with excess of zinc solution, is then spread evenly upon filter-paper, several layers thick; when the paper has absorbed most of the solution, the moist white layer of sulphide of zinc is ready for use.

According to Field, the most expeditious method of converting protosalts of copper into subsalts by means of alkaline sulphites, is to mix about equal quantities of sulphite and carbonate of soda, and to make of these salts a strong cold solution. This liquid poured into a protosalt of copper, instantly decomposes it. After a few minutes' boiling, the whole is converted into suboxide, which dissolves in hydrochloric acid or ammonia without a shade of colour.

Separation of Oxide of Copper from Oxide of Lead :—

(1.) *By Cyanide of Potassium.*—To the diluted solution of the two oxides, carbonate of soda is added in slight excess, and then cyanide of potassium, and heat applied. The lead precipitates as carbonate; the copper remains in solution in the form of double cyanide of copper and potassium : it is evaporated with sulphuric acid till all the hydrocyanic acid is expelled, then largely diluted with water, and precipitated at the boiling temperature by caustic potassa.

(2.) *By Sulphuric Acid.*—The solution is concentrated, and the oxide of lead precipitated by dilute sulphuric acid, the sulphate of lead is collected on a filter, and washed first with dilute sulphuric acid, and then with spirits of wine. The filtrate is boiled for some time, to drive off the alcohol, and finally precipitated by caustic potassa.

Separation of Oxide of Copper from Oxide of Silver :—

(1.) *By Hydrochloric Acid.*—Nitric acid is added to the solution, the silver is then precipitated as chloride, by hydrochloric acid, and the oxide of copper is thrown down from the filtrate by caustic potassa.

(2.) *By Cyanide of Potassium.*—The solution is neutralized with potassa, cyanide of potassium is then added till the precipitate which is first formed is entirely redissolved. To the clear solution nitric acid is added, which precipitates the silver completely as cyanide. The filtrate is evaporated with sulphuric acid till all the hydrocyanic acid is expelled, and the copper is finally precipitated by caustic potassa. Fresenius gives another method of treating the solution of the oxides of these two metals in cyanide of potassium. Sulphuretted hydrogen is passed into the solution, which precipitates only the silver, provided sufficient cyanide of potassium be present. The solution filtered from the sulphide of silver is heated to expel the excess of sulphuretted hydrogen; cyanide of potassium is again added, and then, having completely decomposed this salt by evaporating with a mixture of sulphuric and nitric acids, the copper is precipitated by caustic potassa.

(3.) Berlandt (Archiv für Pharm., Band clv. 279) dissolves the mixed metals in nitric acid, and evaporates the solution to dryness, to get rid of excess of acid. He then dissolves one ounce of the salts in five ounces of water, filters the solution, adds fourteen ounces of a solution of protosulphate of iron (five and a half parts sulphate to eight and a half parts water) mixes, and stirs well. The greyish-white deposit, washed with very dilute sulphuric acid, and afterwards with water, is found to be pure silver.

For the various methods of assaying alloys of silver and copper, see "SILVER."

Separation of Oxide of Copper from Oxide of Mercury :—

(1.) *By Cyanide of Potassium.*—This is effected in the same manner as the separation of oxide of silver from oxide of copper; the solution of the two oxides in cyanide of potassium is treated with sulphuretted hydrogen, by which mercury alone is precipitated.

(2.) *By Formiate of Soda.*—Hydrochloric acid is added to the solution, which is then nearly neutralized with potassa, and the mercury precipitated as subchloride by formiate of soda, in the manner directed in treating of the separation of oxide of mercury from oxide of cadmium.

Separation of Oxide of Copper from Oxide of Bismuth :—

(1.) *By Carbonate of Ammonia.*—On adding this reagent to the solution of the two oxides, in considerable excess, oxide of bismuth alone is precipitated; it is allowed to remain at rest

for some time in a warm place, and then filtered, the oxide of bismuth being washed on the filter with carbonate of ammonia. The filtrate is gently evaporated to expel the excess of carbonate of ammonia, caustic ammonia is then added, and the oxide of copper is finally precipitated by caustic potassa. This method is not to be recommended, it being difficult to remove all traces of oxide of copper from the precipitated oxide of bismuth, even by protracted washing with carbonate of ammonia.

(2.) *By Cyanide of Potassium.*—Carbonate of soda is first added in slight excess to the solution, the oxide of bismuth is then precipitated in the form of carbonate, by heating with cyanide of potassium; the copper in the filtrate is determined by precipitating it by caustic potassa, having previously expelled the hydrocyanic acid by evaporating with sulphuric acid.

(3.) *By Chlorine.*—The solution of the two metallic oxides is precipitated by sulphuretted hydrogen, and the mixed sulphides, having been washed and weighed, are introduced into a bulb, blown in a tube of hard glass, connected with an apparatus for generating chlorine. A stream of this gas is transmitted through the tube, which at the same time is heated by a spirit lamp, first gently, and then to redness; the sulphides are thus converted into chlorides, and the chloride of bismuth, being volatile, is gradually expelled; it may be received into a vessel containing water impregnated with hydrochloric acid, or the amount of oxide may be estimated by the loss of weight sustained by the analysed substance. The apparatus employed may be the same as that used for separating mercury from lead, mercury from silver, or bismuth from lead. The chloride of copper remaining in the bulb is washed out with a little dilute nitric acid, evaporated with sulphuric acid, and finally precipitated by caustic potassa.

Separation of Oxide of Copper from Oxide of Cadmium:—

(1.) *By Carbonate of Ammonia.*—This reagent is added in excess to the solution of the two oxides; carbonate of cadmium is precipitated, while oxide of copper remains in solution.

(2.) *By Cyanide of Potassium.*—This reagent is added until a clear solution is obtained, sulphuretted hydrogen is then passed through the mixture, by which the *cadmio-cyanide* is completely decomposed, sulphide of cadmium being precipitated, while the whole of the sulphide of copper remains in solution. The excess of sulphuretted hydrogen is expelled by heat, and a little more alkaline cyanide added. The copper may then

be precipitated as sulphide, by the addition of an acid; or the double cyanide may be decomposed by evaporating with sulphuric acid, and the metal precipitated as oxide by caustic potassa.

(3.) *By Iodide of Potassium* (Pisani).—The copper is precipitated as iodide, by the addition, first of sulphurous acid, a gentle heat being applied, and then of iodide of potassium until the supernatant fluid has lost the colour due to the presence of copper, and the formation of a precipitate ceases. From the filtered liquor the cadmium is precipitated by sulphuretted hydrogen.

(4.) The metals are precipitated as sulphides, the sulphides are boiled with dilute sulphuric acid (one part concentrated acid, and five water) and rapidly filtered. The filtrate contains the whole of the cadmium, which may then be precipitated by sulphuretted hydrogen.

Separation of Oxide of Copper from Oxide of Zinc: Analysis of Brass.—Although oxide of zinc is, when alone, completely soluble in caustic potassa, this reagent cannot safely be employed to separate zinc from copper, since the oxide of copper invariably carries down with it a greater or lesser quantity of oxide of zinc. Sulphuretted hydrogen is, however, an effectual reagent for this purpose.

(1.) The alloy, being dissolved in nitric acid, is treated with a current of the gas; sulphide of copper alone precipitates, and from the filtrate the oxide of zinc may be completely thrown down, by boiling with carbonate of potassa or by evaporating it to dryness, and igniting in a platinum crucible.

(2.) The copper is precipitated by sulphurous acid and iodide of potassium, according to Pisani's method, and the zinc in the filtrate, by carbonate of soda or potassa.

(3) *MM. Rivot and Bouquet's method.*—The alloy is dissolved in nitric acid, diluted with water, and saturated with ammonia. Into the ammoniacal solution is now put a slight excess of pure potassa in fragments, and the whole is gently heated on a sand-bath until it is completely decolorized, and until the liquor no longer smells of ammonia. The oxide of copper is now thrown on a filter, and washed with boiling water. Into the alkaline liquor hydrochloric acid is poured, until the whole displays an acid reaction, when the zinc is precipitated by carbonate of soda. Before filtration, the solution is heated during seven or eight hours on a sand-bath, for the purpose of

eliminating free carbonic acid. The precipitate is now filtered, washed with boiling water, separated from the filter, and calcined. The two metals are thus estimated in the state of oxide.

Separation of Copper from Nickel. (Dewilde, 'Bulletin de la Société Chimique de Paris.')—Dissolve about 30 grains of the alloy in hydrochloric acid with the addition of nitric acid; evaporate the excess of acid, and dissolve the chlorides in about two pints of water. To the solution add pure cream of tartar, double the weight of the alloy. Heat slightly to favour the solution, and add, little by little, a solution of caustic potassa in alcohol. The metals are precipitated as hydrates, which are redissolved by an excess of the alkali. The blue liquid is boiled for a few minutes with a solution of grape sugar; the copper is hereby precipitated as suboxide, which is washed, dried, and calcined, and then converted into nitrate, and the copper estimated by one of the volumetric methods. The filtered solution containing the nickel is evaporated to dryness, the residue incinerated, then washed to remove the carbonate of potassa, and a second time incinerated and washed, it is then redissolved in aqua-regia from which the hydrated oxide is precipitated by potassa. As it is very difficult thoroughly to wash this voluminous hydrate, Dewilde prefers, where great accuracy is required, to dry, calcine, and then after another washing with hot water, to reduce it to metallic nickel in a platinum crucible in an atmosphere of hydrogen gas.

Detection and estimation of small quantities of Antimony, Arsenic, Bismuth, and Lead in metallic Copper :—

Analysis of Commercial Copper. (Abel and Field, Quart. Journ. Chem. Soc., January, 1862.)

(a.) *Determination of Antimony and Arsenic.*—Two hundred grains of the metal are dissolved in nitric acid, a small quantity of solution of nitrate of lead is added, equal to about ten grains of the salt, and subsequently an excess of ammonia and carbonate of ammonia. A precipitate is formed which may consist of oxide and carbonate of lead, *arsenate* and *antimoniate of lead*, and oxide of bismuth, the whole of the copper remaining in solution. The precipitate is separated by filtration, thoroughly washed, and digested in a strong solution of oxalic acid, whereby the *antimony* and *arsenic* are dissolved. To the filtered liquid sulphide of ammonium is added, or what is preferable, it is rendered alkaline by ammonia, and hydrosulphuric acid passed through to saturation. Traces of sulphide of copper generally

impart a greenish tinge to the liquid, and are deposited after some time, as it is nearly impossible to wash away the last traces of that metal, from the nitrate of lead precipitate. This sulphide is filtered off, and a slight excess of hydrochloric acid is added to the filtrate which is diluted to about 8 ounces. If any large amount of either antimony or arsenic be present, there will be an immediate precipitate. If smaller quantities exist (one or two-hundredths of a grain), the flask should be placed on the sand bath for a few hours and the temperature maintained at from 140° to 200° F., when the metals, if present, will make their appearance as sulphides. If the precipitate be orange or orange-red, the presence of antimony is certain; but if a pure canary-yellow, its absence may be presumed. The precipitated sulphides are oxidized by means of concentrated nitro-hydrochloric acid, the clear solution is mixed with chloride of ammonium and excess of ammonia, and the arsenic is separated as ammonio-magnesian arsenate ($2MgO,NH_4O,AsO_5,HO$). The filtrate from this, is slightly acidified with dilute hydrochloric acid, and the antimony is precipitated by hydrochloric acid, and ultimately determined as antimoniate of teroxide of antimony (SbO_4). Should the presence of antimony and arsenic have been previously ascertained, it is of course unnecessary in the quantitative process, to precipitate them both as sulphides from their solution in oxalic acid, as the arsenic may be at once precipitated by the addition of sulphate of magnesia and excess of ammonia, and the antimony determined in the filtrate.

(b.) *Determination of Lead and Bismuth.*—The nitric acid solution of about 200 grains of the copper is mixed with a small quantity of solution of phosphate of soda; ammonia in excess is then added, and the resulting precipitate is collected and purified from copper, by washing with ammoniacal water. The precipitate is afterwards dissolved in hydrochloric acid, its solution is rendered alkaline with ammonia, and submitted to a current of sulphuretted hydrogen. The precipitated sulphides of lead and bismuth are thoroughly washed and dissolved in dilute nitric acid. The solution is nearly neutralized with ammonia, and then digested with a little hydrated oxide, or basic nitrate of copper, which precipitates the oxide of bismuth, while the lead remains in solution. The precipitate is thoroughly washed, dissolved in dilute nitric acid, and the bismuth separated from the copper by the addition of excess of ammonia. The oxide of bismuth thus obtained is purified by washing, and

its weight determined in the usual manner. The solution containing the nitrates of lead and copper is mixed with solution of carbonate of soda; excess of acetic acid and a small quantity of bichromate of potassa are added, and the chromate of lead is collected. Should the copper contain iron, that metal would be obtained as oxide together with the bismuth. When this is the case, which may readily be known by the brownish tinge imparted to the oxide of bismuth, they must be separated.

An extremely delicate method of testing copper for *bismuth* is the following, founded upon a curious reaction exhibited by iodide of potassium in the joint presence of lead and bismuth, first noticed by Field. About 100 grains of the copper to be examined are dissolved in nitric acid, a solution of nitrate of lead equal to about 5 grains of the salt is added, and subsequently ammonia and carbonate of ammonia. The precipitate is washed with ammoniacal water to free it from copper, and dissolved in warm acetic acid. Considerable excess of iodide of potassium is introduced, and the liquid is warmed until the precipitate disappears. On cooling, crystalline scales make their appearance, which by their colour indicate the presence or absence of bismuth. If that metal be absent, the scales are brilliant gold-colour, but if it be present, or even the slightest trace, they assume a dark orange or crimson tint, varying in intensity of colour according to the amount of bismuth present. If it be desired to test the copper for arsenic, the nitrate of lead precipitate is digested with acetic acid. The oxalates of lead and bismuth are insoluble in acetic acid, but it dissolves the arsenic.

Analysis of a mixture of Oxides of Lead, Bismuth, Silver, Copper, Mercury, and Cadmium.—To a diluted solution, carbonate of potassa is first added, and then excess of cyanide of potassium; the oxides of *lead* and *bismuth* are precipitated in the form of carbonates; they are received on a filter, washed, dissolved in nitric acid, and the oxide of lead separated from the oxide of bismuth by dilute sulphuric acid, as directed (p. 371). The washing from the precipitated carbonates being mixed with the filtrate, excess of diluted nitric acid is added, the silver is precipitated as cyanide, in the form of which salt it is estimated. The filtrate from the cyanide of silver, together with the washings, are again neutralized by carbonate of potassa, a fresh quantity of cyanide of potassium is added, and a stream of sulphuretted hydrogen gas is passed through the

solution, the *mercury* and the *cadmium* are precipitated as sulphides: the whole of the sulphide of copper is retained in solution by the cyanide of potassium, provided a sufficient quantity of that reagent has been added; to ensure this, it is advisable to add a fresh portion after the action of the sulphuretted hydrogen. The precipitated sulphides of mercury and cadmium, after being well washed on the filter, are decomposed by digestion with aqua-regia, the solution is filtered off from the sulphur, nearly neutralized with potassa, and the mercury estimated as subchloride. The cadmium in the solution, filtered from the subchloride of mercury, is precipitated by carbonate of soda. The sulphide of copper, which remains dissolved in the cyanide of potassium, is mixed with nitric acid and evaporated with the addition of sulphuric acid, until the whole of the hydrocyanic acid is expelled; the sulphate of copper retained in solution is finally precipitated at a boiling temperature by caustic potassa.

179. Palladium.

This metal is remarkable for its great affinity for *cyanogen*, on which property is founded a method of separating it from its solutions; *cyanide of mercury* is added, the solution having previously been neutralized with soda; a bright yellow precipitate is produced, which, by drying, becomes yellowish-grey, and by ignition is decomposed, metallic palladium of a blue colour remaining in the crucible. From all metals which are not precipitated by sulphuretted hydrogen, palladium may be separated by that reagent; the resulting sulphide is converted by heat into basic sulphate, which, being dissolved in hydrochloric acid, and neutralized with soda, is precipitated by cyanide of mercury.

Separation of Palladium from Copper.—In crude platinum ores palladium occurs in combination with copper. Berzelius gives the following process for separating these two metals. (Poggendorf's 'Annalen,' Band xiii. p. 561.) Both metals are precipitated from an acid solution by sulphuretted hydrogen. The precipitated sulphides are exposed to heat, while still moist, and roasted as long as they give off sulphurous acid; they are thereby converted into basic sulphates of oxides. These salts are dissolved in hydrochloric acid, the solution is mixed with chloride of potassium and nitric acid, and then evaporated to dryness. The dark saline mass thus produced contains chloride

of potassium, chloride of copper and potassium, and chloride of palladium and potassium. The first two of these salts are to be extracted by alcohol, specific gravity 0·833; the palladium salt, being insoluble therein, remains behind. It is brought on a weighed filter, and washed with alcohol; it is then dried and weighed; it contains 28·84 per cent. of palladium. The saline mass may also be dissolved in water, and precipitated with cyanide of mercury. The alcoholic solution of the copper salt is evaporated to expel the spirit, the saline mass is redissolved in water, and the copper precipitated by caustic potassa.

Palladium has been imported into this country from Brazil, alloyed with gold, some specimens containing 5 or 6 per cent. of palladium. The operation of refining is thus described by Mr. Cock (Proc. Chem. Soc., vol. i. p. 162). The gold dust is fused, in charges of about 7 lbs. troy, with its own weight of silver, and a certain quantity of nitre; the effect of this fusion is to remove all earthy matter, and the greater part of the base metals contained in the gold dust, and in the silver melted with it. The fused mixture is cast into ingot moulds, and when cooled, the flux or scoriæ is detached. Two of the bars thus obtained are then remelted in a plumbago crucible, with such an addition of silver as will afford an alloy, containing one-fourth its weight of pure gold, and which, first being well stirred to ensure a complete mixture, is poured through a perforated iron ladle into cold water, and thus very finely granulated. It is then ready for the process of parting. For this purpose about 25 lbs. of the granulated alloy are placed in a porcelain jar upon a heated sand-bath, and subjected to the action of about 25 lbs. of pure nitric acid, diluted with its own bulk of water; after the action of this quantity of acid, the parting of the gold is very nearly effected; but, to remove the least portions of silver, etc., about 9 or 10 lbs. of strong nitric acid are boiled upon the gold for two hours. It is then completely refined, and, after being washed with hot water, is dried and melted into bars containing 15 lbs. each.

The nitrous gas, and the vapour of nitric acid arising during the above process, are conducted by glass pipes (connected with the covers of the jars) into a long stoneware pipe, one end of which slopes downwards into a receiver for the condensed acid, the other end being inserted into the flue for the purpose of carrying off the uncondensed gas.

The nitrate of silver and palladium, obtained as above, is carefully decanted into large pans, containing a sufficient quantity of solution of common salt to effect the precipitation as chloride, of the whole of the silver, the palladium and copper remaining in solution in the mother-liquor, which is drawn off, and, when clear, run off, together with the subsequent washings from the chloride of silver, into wooden vessels, and the metallic contents are then separated in the form of a black powder, by precipitation with sheet zinc, assisted by sulphuric acid. The chloride of silver, when washed clean, is reduced by the addition of granulated zinc and dilute sulphuric acid, washed on the filter with boiling water, dried, and melted in plumbago crucibles, without the addition of any flux. From the black powder obtained as above, the palladium is extracted by re-solution in nitric acid and supersaturation with ammonia, by which the oxides of palladium and copper are first precipitated and then redissolved, while those of iron, lead, etc., remain insoluble. To the clear ammoniacal solution, hydrochloric acid in excess is then added, which occasions a copious precipitation of the yellow ammonio-chloride of palladium, from which, after sufficiently washing it with cold water and ignition, pure metallic palladium is obtained. The mother-liquor and washings contain all the copper and some palladium, which are recovered by precipitation with iron.

180. Rhodium.

This metal is, according to Berzelius, (Poggendorff's Annal., Band xiii. p. 254) best estimated by the following process:—The solution is mixed with excess of carbonate of soda, and evaporated to dryness; the dry residue is then ignited in a platinum crucible. Upon dissolving the mass in water, peroxide of rhodium remains behind, which is brought upon a filter, and washed, first with hydrochloric acid, and finally with water. It is then ignited with the filter, and subsequently reduced by hydrogen gas. The reduction is so easily effected, that it is scarcely necessary to assist the action of the gas by the application of heat.

Separation of Rhodium from Copper.—Berzelius directs to pour the solution into a flask which is furnished with a glass stopper, and to saturate it with sulphuretted hydrogen gas. The flask is then closed and allowed to remain for twelve hours in a warm situation. The sulphide of copper is, in that time

fully, and the sulphide of rhodium, for the most part, precipitated. The solution is filtered, and, being heated and evaporated, yields a fresh portion of sulphide of rhodium, which is added to the other sulphides. These are placed, while still moist, in a platinum crucible, and roasted as long as sulphurous acid exhales. When the roasting is finished, the mass is subjected to the action of concentrated hydrochloric acid, peroxide of rhodium remains undissolved, and is reduced by hydrogen gas; the copper in the solution is precipitated by caustic potassa.

Rhodium exists together with *iridium*, *palladium*, *osmium*, etc., in platinum ores. It is extracted from the liquor from which the palladium has been precipitated by cyanide of mercury, by the following process. Hydrochloric acid is added, and the solution is evaporated to dryness, the excess of cyanide of mercury is decomposed, and transformed into chloride. The dry saline mass is reduced to a very fine powder and washed with alcohol, sp. gr. 0·837. The double chlorides of sodium and platinum, sodium and iridium, sodium and copper, and sodium and mercury, are dissolved, but the double chloride of sodium and rhodium remains behind in the form of a fine red powder. It is washed with alcohol and decomposed by gently heating in a current of hydrogen gas, by which the chloride of rhodium is reduced, and the metal is subsequently separated from the chloride of sodium by water. Another method of treating the saline mass is to mix it with about twice its weight of carbonate of potassa, and to calcine the mixture. The residue is treated with water, and the copper dissolved out by hydrochloric acid. The residual mass is next mixed carefully with five times its weight of anhydrous bisulphate of potassa and heated to redness in a well-covered platinum crucible; the heat is continued till the mixture is about to solidify. The oxide of rhodium dissolves in the bisulphate of potassa. The saline mass is extracted with boiling water, and the process is repeated with fresh bisulphate as long as the salt continues to receive colour; excess of carbonate of soda is poured into the aqueous extract, the whole is evaporated to dryness, and the residue is calcined; the residue is again treated with boiling water; oxide of rhodium remains undissolved, and is then in a state to be reduced by hydrogen gas.

181. Osmium and Ruthenium.

The first of these metals, which is found in combination with *iridium* in platinum ores, is extracted by the following process (Berzelius's 'Traité de Chimie'):—The grains of *osmium-iridium*, which are exceedingly hard, are reduced to a very fine powder, which is then digested with hydrochloric acid, to remove the iron which has become rubbed from the mortar during the operation of trituration; it is then dried, mixed with nitre, and heated gradually to redness in a porcelain retort connected with a receiver containing caustic ammonia. During this operation both metals become oxidized, and a portion of the oxide of osmium, or osmic acid, which is volatile, is carried forward with the nitric oxide gas, and condensed in the ammonia, to which it communicates a yellow colour. Another portion is condensed on the sides of the receiver in the form of a crystalline mass. All disengagement of gas having ceased, the apparatus is allowed to cool, the receiver containing the ammonia is then removed, and the mass which remains in the retort is dissolved in water. The solution is of a deep-brown colour, and contains a combination of the two oxides with potassa. It must not be filtered, since the organic matter of the paper decomposes it. It is therefore at once distilled, at a gentle heat, in a retort connected with a receiver, and the greater part of the liquor drawn over. This liquor, which is colourless, and possessed of a strong and disagreeable odour, contains the osmium in the form of *osmic acid*. The following method of extracting *iridium* and *osmium* from the pulverulent residue, after digesting platinum ore with aqua-regia, was proposed by Wöhler. The residue is mixed with an equal weight of dry and finely pulverized common salt, heated to redness in a long glass tube, and a stream of chlorine sent through, as long as it continues to be absorbed. In this operation, the *titanate of iron* is not attacked, but there are formed compounds of iridium and osmium with chloride of sodium; much osmic acid is also disengaged, being expelled with the aqueous vapour introduced with the chlorine gas; this is condensed in a receiver containing ammonia, which is adapted to the tube. When no more chlorine is absorbed, the contents of the tube are treated with water, which dissolves the double salts of iridium and osmium. The solution has a deep red-brown colour. The

titanate of iron and other matters remain undissolved. The solution is then distilled, by which much osmic acid, arising from the decomposition of the chloride of osmium, is removed, and is condensed in a receiver containing ammonia; when no more osmic acid passes over, the distillation is stopped, and the residual liquor, after being filtered, is mixed with excess of carbonate of soda, evaporated to dryness, and the residue feebly calcined. It consists of a mixture of suboxide of iridium with chloride of sodium; the latter is dissolved out by water. The suboxide of iridium is not, however, pure, it still contains a notable quantity of iron and of osmium; the former is removed by reducing the oxide to the metallic state in a current of hydrogen gas, and then acting on the residue with concentrated hydrochloric acid. Under this treatment the platinum residue loses in general from 25 to 30 per cent. of its weight; it is not, however, exhausted; and, by a second treatment with chloride of sodium, a further amount of 5 or 6 per cent. of a mixture of osmium, iridium and iron may be extracted. From the residue a small quantity of platinum may generally be dissolved out by aqua-regia; it not unfrequently also contains chloride of silver, which may be separated by ammonia.

The following modification of this process has been recommended by Fritzsche (Journ. für Prakt. Chem., xxxvii. p. 483):—Equal portions of caustic potassa and chlorate of potassa are melted together in a very spacious porcelain crucible over a spirit-lamp, and into the fused mass is conveyed about three times its weight of osmium-iridium, without first reducing it to powder. As soon as, on further heating, the chlorate of potassa liberates oxygen, the fused mass begins to act on the osmium-iridium. The mass froths violently, so that the heat must be moderated when it becomes more tenacious; the action at last proceeds without any further heating, the mass becomes nearly black, and the operation is discontinued as soon as the frothing has ceased. During the whole operation not a trace of osmium vapours is perceptible, but a slight evolution commences on the solidification of the mass, which is increased by further heating; this, however, is unnecessary, so that there is scarcely any trouble with the vapours of osmic acid. Six hundred grammes of osmium-iridium may be fused with ease in a porcelain crucible capable of holding 2 lbs., with 100 grammes of caustic potassa and chlorate of potassa, over a spirit-lamp. The operation scarcely lasts an

hour, and at least 50 grammes are decomposed. On treating the fused mass with water, an orange-coloured solution, containing *osmium* and *ruthenium*, is obtained, and a blackish-blue precipitate, which may very easily be separated by suspension from the undecomposed *iridium-osmium*.

By the above process of Berzelius, iridium cannot be completely separated from osmium, for, on heating the former while exposed to the air, vapours of osmic acid are always disengaged. In order to complete the separation of these two metals, the following method is employed by Fremy ('Comptes Rendus,' Jan. 22, 1844):—100 grammes of the residue of the platinum workings are mixed with 300 grammes of nitre; the mixture is introduced into a large crucible and kept for an hour at a red-heat in a wind furnace. After this calcination the mass is poured on a metallic plate, which operation should be performed in the open air, and it is even indispensable to cover the face, for without this precaution the vapours of osmic acid would act violently on the skin. During the calcination with nitre, a certain quantity of osmic acid is lost, but it was found that the proportion of this acid which might be condensed would never repay the inconveniences of calcining in a porcelain crucible. The decanted mass, which contains the osmiate and iridiate of potassa, is treated in a retort with nitric acid, which liberates the osmic acid, which is condensed in a concentrated solution of potassa. The residue is treated with water, which removes the nitre, and it is then acted upon with hydrochloric acid, which dissolves the oxide of iridium. In this manner the osmium is obtained in the state of osmiate of potassa, and the iridium in that of soluble chloride. Into the solution of osmiate of potassa Fremy pours a small quantity of alcohol; the liquid becomes heated, acquires a red tint, and deposits a crystalline powder of *osmite* of potassa; in this case the osmium is frequently precipitated entirely from solution. The salt may be washed with alcohol, which does not dissolve it, and it then may be preserved without alteration. All the compounds of osmium may be prepared from it. On treating it with a cold solution of sal-ammoniac, it dissolves at first, and is then decomposed, giving rise to a new yellow salt, scarcely soluble in cold water. This salt, which is so easily prepared, affords, on calcination in a current of hydrogen, perfectly pure osmium.

To extract the *iridium*, Fremy treats the chloride obtained

as above with sal-ammoniac, a reddish-brown precipitate is formed, consisting of a combination of the bichlorides of osmium and iridium with sal-ammoniac. To separate these two double salts a stream of *sulphurous acid* is passed into the water in which they are suspended, the double salt of iridium is decomposed, chloride of iridium is formed, which is very soluble in water; the double salt of osmium undergoes no change, it remains in the state of a red salt. The soluble salt of iridium crystallizes in large brown prisms out of solutions in sal-ammoniac; it is therefore easy to purify it when calcined in a current of hydrogen; it affords metallic iridium in a state of purity.

Besides *iridium* and *osmium*, another metal has been found in the platinum residues by Professor Clauss (Bullet. de la Classe Physico-Math. de l'Acad. de St. Pétersbourg, t. iii. p. 311). It is called by its discoverer *ruthenium*. He prepared it in the following manner:—The residue, which had been once fused with nitre and extracted with water and acids, was mixed with an equal quantity of nitre, and kept at a white-heat in a Hessian crucible for two hours. The mass was taken out while still red-hot, with an iron spatula, and, after cooling, was reduced to a coarse powder, which was extracted with distilled water, leaving it to stand with it till it became clear; the perfectly clear liquid, which was of a dark yellow colour, was then decanted. It could not be filtered, since it was decomposed by the action of the organic matter of the paper. It contained *rutheniate*, *chromate*, and *silicate* of potassa, not a trace of either *rhodium* or *iridium*, and only a very minute trace of *osmiate of potassa*. Nitric acid was cautiously added to this solution, until the alkaline reaction of the liquid had disappeared: oxide of ruthenium and potassa, and some silicic acid, were hereby precipitated in the form of a velvet black powder, while chromate of potassa remained undissolved. After edulcoration, the oxide of ruthenium and potassa was dissolved in hydrochloric acid, and the solution was evaporated till the silica separated as a gelatinous mass. It was then diluted with water and filtered. It could not be evaporated to dryness for the more complete separation of the silica, because the chloride of ruthenium was thereby decomposed into an insoluble protochloride. The filtered solution, which is of a very beautiful orange-yellow colour, was evaporated down to a very small volume, and mixed with a concen-

trated solution of chloride of potassium, when the salt $KCl + RuCl_4$ separated in reddish-brown crystals. A further quantity was obtained by evaporating the liquid decanted from the crystals. The salt was further purified by recrystallization. Clauss has hitherto only been able to obtain the metal as a blackish-grey powder, which is considerably lighter than *iridium:* the aqueous solution of the chloride is precipitated in the form of a black oxide by ammonia, by which it is distinguished from all the other platinum metals, none of which are precipitated by ammonia at the ordinary temperature. If a slip of zinc be inserted in the solution of the orange-coloured chloride acidified with hydrochloric acid, a black metallic powder is after a time deposited, the liquid acquires a dark indigo-blue colour, but subsequently, after the whole of the metal is deposited, becomes colourless.

GROUP V.—Section B.

Antimony, Arsenic, Tin, Platinum, Iridium, Gold, Selenium, Tellurium, Tungsten, Molybdenum, Titanium.

182. Antimony.

This metal is quantitatively estimated as *sulphide*, as *antimonious acid*, and as *pure metal.*

Precipitation as Sulphide.—The solution is diluted with water, and sufficient tartaric acid added to redissolve any basic salt, which the addition of water may have precipitated. A stream of washed sulphuretted hydrogen gas is then conducted through the solution until it smells strongly of it; it is allowed to remain at rest for some time in a moderately warm situation, till the excess of sulphuretted hydrogen has been expelled. If the solution under examination contain antimony in the state of oxide only, the precipitated sulphide may be then collected on a weighed filter, washed thoroughly with distilled water, dried at 212°, and weighed. Its composition is

One equivalent	of Sb	. .	120	. . 71·43
Three ditto	of S	. . .	48	. . . 28·57
One ditto	of SbS_3	.	168	. . 100·00

But if any of the higher oxides of antimony are also present, which will always be the case when the compound under examination is dissolved in aqua-regia, correct results cannot be obtained by simply weighing the precipitated sulphide, its composition being variable. In this case the sulphide must be decomposed by nitric acid, and the amount of sulphur present determined by converting it into sulphuric acid in the following manner:—The sulphide is collected on a filter, dried at 212°, and its weight, filter included, accurately determined; a portion is then removed for analysis, the weight of this portion is noted; it is digested in a flask with fuming nitric acid, carefully added at first, the action generally being very energetic; hydrochloric acid is then added, and heat applied and continued for some time; if a clear solution be obtained, it is diluted with water, tartaric acid being added to redissolve any basic salt which may be thereby precipitated. The sulphuric acid formed by the oxidation of the sulphur is precipitated in the form of sulphate of baryta by chloride of barium: it is received on a filter, well washed with boiling distilled water, ignited, and weighed: from the weight obtained, the amount of sulphur is calculated, which, being deducted from the weight of the sulphide of antimony operated on, gives the quantity of metal; should it happen that a portion of the sulphur escaped oxidation by the nitric acid, the solution will not be clear; in this case, the solution, having been diluted with water with the requisite addition of tartaric acid, is passed through a weighed filter, and the weight of the separated sulphur, after being well washed and dried on the filter at 212°, is added to that calculated from the sulphate of baryta. It may be observed, that it is easy to see whether sulphide of antimony precipitated from the original solution by sulphuretted hydrogen is the sulphide corresponding to SbO_3: a small weighed portion of it is boiled in a test tube with hydrochloric acid, if a clear solution be obtained, the sulphide is SbS_3, and the remainder may at once be weighed and calculated, but if it do not completely dissolve, it contains a mixture of one or more of the higher sulphides, and the residue must be treated as above directed. Two other methods have been proposed for treating the mixed sulphides: one is to decompose them at a gentle heat in a current of dry hydrogen gas, by which operation the sulphur is removed partly as sulphur, and partly as sulphuretted hydrogen, metallic antimony being left behind; the other is to

heat the mixture in a small retort out of contact of air, by which all the higher sulphides are converted into the lowest; neither of these methods, however, gives such correct results as the first. When the reduction process is adopted, it is impossible to regulate the heat so as to prevent the volatilization of a small portion of the antimony, and, in the process of heating the sulphides out of contact of air, a portion of SbS_3 is volatilized, and another portion is reduced to oxide, which is sublimed together with the sulphur.

Estimation as Antimonious Acid.—The compound is evaporated with nitric acid, and the residue ignited as long as it continues to lose weight: its composition is:—

One equivalent of Sb	. . .	120	. . 78·94
Four ditto of O	. . .	32	. . 21·06
One ditto of SbO_4	. .	152	. . 100·00

Dilute solutions of antimony in which the amount of metal is to be determined, must not be concentrated by evaporation when they contain hydrochloric acid, as is almost always the case, because terchloride of antimony escapes with the vapour of acid. The volatilization of the metal cannot be prevented by the addition of sulphuric acid, but it may be, pretty nearly, by nitric acid. The estimation of sulphur in precipitated sulphide of antimony may be made by treating a weighed quantity of it with hydrochloric acid; terchloride of antimony ($SbCl_3$), corresponding in composition to teroxide of antimony (SbO_3), is formed, and the equivalent quantity of sulphur escapes in the form of sulphuretted hydrogen. The remainder of the sulphur separates in the solid form, and after boiling with hydrochloric acid it may be collected on a filter, washed first with water, containing some hydrochloric and tartaric acids, and lastly with pure water; its weight indicates the amount of the sulphide of antimony (Rose).

Assay of Antimony Ores (Levol, Ann. de Chim. et de Phys., 3 ser. xlvi. p. 472).—100 parts of the ore (the sulphide) are mixed with 200 of ferrocyanide of potassium (anhydrous), covered with 50 parts of cyanide of potassium, and heated to a dull red-heat in an iron crucible; a regulus of metallic antimony is obtained, which, according to the author, represents nearly exactly the quantity contained in the ore. Ores of lead may be assayed in a similar manner.

183. Arsenic.

This metal may be quantitatively estimated as *arsenic acid* by combining it with *oxide of lead*, and as *ammonio-arsenate of magnesia;* it may also be conveniently weighed as *sulphide*.

Quantitative estimation by Protoxide of Lead.—To ensure the metal being in the state of arsenic acid, the compound under examination (which must contain no other acid) is digested with aqua-regia, and carefully evaporated to dryness; the residue, after being somewhat more strongly heated in a platinum crucible, is dissolved in water, and a known weight of recently ignited and pure protoxide of lead added; the mixture is carefully evaporated to dryness, and gently ignited: the amount of arsenic acid present, is learnt from the increase in weight, and from this the quantity of arsenic is calculated.

Estimation as Sulphide.—For this purpose the arsenic must be in the form of *arsenious acid,* to ensure which, the solution of the compound should be mixed with a concentrated aqueous solution of *sulphurous acid*, and gradually heated to gentle ebullition in a flask; the heat must be maintained till the whole of the excess of sulphurous acid is expelled; hydrochloric acid is now added, and a stream of washed sulphuretted hydrogen is conducted through the liquid, till it smells strongly of it. It must not be immediately filtered, because the sulphuretted hydrogen liquor may hold in solution a portion of sulphide of arsenic. It is set aside in a warm place, until the excess of sulphuretted hydrogen gas is expelled. Fresenius recommends that this be done by transmitting through the solution a stream of washed carbonic acid gas. The liquid being freed from sulphuretted hydrogen, is passed through a weighed filter, washed with hot distilled water, dried at 212°, and weighed. Its composition is—

One equivalent of As	75	60·97
Three ditto of S	48	39·03
One ditto of AsS_3	123	100·00

Should the process of treating the solution with sulphurous acid not have been adopted, and if there is reason for supposing that a portion of the arsenic may have been in a higher state of oxidation than that of arsenious acid, and if, moreover, there should be present certain other substances capable of decomposing sulphuretted hydrogen, such as *chromic acid, peroxide*

of iron, etc., then the sulphide of arsenic cannot be weighed for the purpose of estimating the metal, until after the excess of sulphur has been removed: this is done precisely in the same manner as has been directed in the case of sulphide of antimony with excess of sulphur, viz. by converting the free sulphur into sulphuric acid, and determining its amount in the form of sulphate of baryta.

A solution of pentasulphide of arsenic (AsS_5) in sulphide of ammonium yields instantly a precipitate of ammonio-arsenate of magnesia with a solution of magnesia. According to Lessen (Ann. der Chem. und Ph.), sulphides of tin and antimony are not precipitated under the same conditions.

Estimation as Arsenate of Magnesia and Ammonia.—For this purpose the arsenic must be in the form of arsenic acid, to which, if in a lower state of oxidation, it must be brought by warming the solution with hydrochloric acid, and then adding chlorate of potassa in small quantities at a time, till the fluid smells strongly of chlorous acid; it is then allowed to cool, ammonia in excess added, and then a mixture of chloride of ammonium and sulphate of magnesia; the solution is allowed twelve hours thoroughly to precipitate, and is then filtered through a weighed filter, the precipitate washed with ammoniacal water, dried at 212° F., and weighed. Its composition is—

Two equivalents of MgO	40·32	21·18
One ditto of NH_4O	26·00	13·66
One ditto of AsO_5	115·00	60·43
One ditto of HO	9·00	4·73
One ditto of ($2MgO,NH_4O,AsO_5,HO$)	190·32	100·00

As the mixture of chloride of ammonium, sulphate of magnesia, and ammonia, is of constant use in the laboratory for the determination of phosphoric acid, it should be kept ready prepared by dissolving 1 part of crystallized sulphate of magnesia and 1 part of chloride of ammonium in 8 parts of water and 4 parts of solution of ammonia, allowing the fluid to stand at rest for several days, and then filtering (Fresenius).

According to Rose (Poggendorff's 'Annalen der Physik und Chemie,' vol. cxvi. p. 453) the arsenates of *iron*, *manganese*, *zinc*, *lead*, and *copper* may be successfully analysed by calcination with sulphur in a current of hydrogen, the arsenic volatilizing as sulphide, the base remaining under the form of fixed

sulphide. In many instances arsenic acid may be expelled from arsenates by calcination with chloride of ammonium; the alkaline arsenates are transformed into chlorides by a single calcination, the earthy arsenates offer more resistance, and in the case of arsenate of magnesia the arsenic acid is never completely expelled. The analysis of native arsenate of iron may be perfectly effected by sulphuretted hydrogen: a weighed quantity of the ore is heated to faint redness in a current of the gas; both metals are converted into sulphides; the sulphide of arsenic is completely volatilized, and the sulphide of iron, which does not contain a trace of arsenic, is dissolved in hydrochloric acid, peroxidized by chlorate of potassa, and precipitated by ammonia.

Separation of Arsenious from Arsenic Acid (Fresenius).—The solution containing the two acids is divided into two equal portions; in one, the arsenic acid is reduced to arsenious acid by sulphurous acid, and the whole then precipitated by sulphuretted hydrogen: the precipitated sulphide of arsenic is washed, dried at 212°, and weighed. The arsenious acid in the other half of the solution is converted into arsenic acid by chlorine, for which purpose it is mixed with hydrochloric acid, and solution of indigo added till the fluid acquires a blue colour. Chloride of lime, containing a known amount of chlorine, is then added from a weighed solution, until the blue colour disappears: from the quantity consumed, the amount of chlorine used is calculated. This operation depends on the circumstance, that every equivalent of arsenious acid requires two equivalents of chlorine to convert it, in the presence of water, into arsenic acid: thus—

$$AsO_3 + 2Cl + 2HO = AsO_5 + 2HCl.$$

By calculating the resulting quantity of arsenious acid upon sulphide of arsenic, and subtracting the weight of this from the total weight obtained from the first portion of the solution, the amount of arsenic acid originally contained in the latter is found. A simpler method is to precipitate the arsenic acid as arsenate of magnesia and ammonia, and to determine the amount of arsenious acid in the filtrate by sulphuretted hydrogen.

Separation of Arsenic from Antimony.—When the compound of the two metals is in the reguline state, the arsenic may be expelled by heating out of contact of air; when, however, other metals are also present, this process cannot be adopted, since

most other metals retain a part of the arsenic when at a red-heat. In this case several methods have been proposed:—

(1.) The substance is dissolved in aqua-regia, tartaric acid is added, the solution is dissolved, and the antimony and arsenic are together precipitated by sulphuretted hydrogen: the sulphides are intimately stirred together, collected on a filter, dried at a very gentle heat, and weighed. From a weighed portion, the amount of sulphur is determined by dissolving it in aqua-regia, and having added tartaric acid and diluted with water, precipitating the sulphuric acid formed by chloride of barium. Another weighed portion of the mixed sulphides is heated in a tube, through which a stream of hydrogen gas is passing; the excess of sulphur and the sulphide of arsenic are expelled, leaving the sulphide of antimony, which may then be weighed. This method, when carefully performed, is capable, according to Rose, of affording a result only about a half per cent. from truth; the proportion of arsenic present is calculated from the loss, the united weight of both metals having by the first experiment been determined in the state of sulphide.

(2.) *Behren's method.*—The arsenic and antimony are converted into sulphides, and to the mixture is added, while still moist, an equal volume of neutral *nitrate of lead*, and about as much water. The mass is boiled in a porcelain dish, being stirred without interruption, and, the water which evaporates being renewed until the whole has acquired a dark-brown colour, it is then filtered. The residue contains the entire amount of antimony, and a portion of the arsenic. The solution contains the arsenic in the state of arsenious acid, nitric acid, and oxide of lead; it is heated with carbonate of ammonia, as long as a precipitate is formed. To the liquid filtered from the carbonate of lead, some hydrochloric acid is added, until it has an acid reaction; sulphuretted hydrogen gas is then transmitted through the solution, and the sulphide of arsenic thus obtained has no trace of antimony. To separate the arsenic contained in the state of sulpharsenide of lead, in the mass which remained on the first filtration, M. Behren digests it at a gentle heat with caustic ammonia, which converts the sulpharsenide of lead into sulphide of lead, and sulphide of arsenic, which latter dissolves in ammonia. To the filtered solution, hydrochloric acid is added, and the sulphide of arsenic precipitated, is added to that first obtained.

Fresenius objects to the precipitation of the lead in the so-

lution containing the arsenic by carbonate of ammonia; he prefers separating the two metals by sulphide of ammonium, or by evaporating the solution to dryness, and fusing the residue with carbonate of soda and nitre.

(3.) *Antimony* and *arsenic* in alloys may, according to Fresenius, be separated, though not in a very accurate manner, by heating the mixture covered with common salt and carbonate of soda, in a glass tube, through which a current of dry carbonic acid gas is passing; the tube is heated gently at first, but the heat is gradually increased to the highest degree of intensity: by this means the arsenic is driven off, while the volatilization of the antimony is prevented by the common salt and carbonate of soda.

(4.) *Hofmann's method* (Quart. Journ. Chem. Soc.).—This is based upon the dissimilar deportment of arseniuretted and antimoniuretted hydrogen with nitrate of silver, the former yielding arsenious acid which passes into solution—

$$H_3As + 6(AgO,NO_5) + 4HO = 6(HO,NO_5) + 6Ag + HO + AsO_3,$$

the latter giving rise to the formation of antimoniuret of silver, which is insoluble in water—

$$H_3Sb + 3(AgO,NO_5) = 3(HO,NO_5) + Ag_3Sb.$$

This process presents no difficulty as far as the arsenic is concerned, which may be recognized in solution by ammonia if there be an excess of silver, or by sulphuretted hydrogen if the silver has been entirely precipitated. It is far less easy to find, according to this process, minute quantities of antimony in the presence of large quantities of arsenic, the silver compound of antimony being mixed with a bulky precipitate of metallic silver. By treating this precipitate with hydrochloric acid, there dissolves, together with the antimony, a small quantity of chloride of silver, which is sufficient to darken the precipitate produced in the solution by sulphuretted hydrogen to such a degree as altogether to mask the presence of antimony. This inconvenience may easily be obviated by boiling the mixture of silver and antimoniuret of silver, after the arsenious acid has been carefully washed out with boiling water, with *tartaric acid*, which dissolves the antimony alone. The solution thus obtained yields at once with sulphuretted hydrogen the characteristic orange-yellow precipitate of sulphide of antimony. In evolving the hydrogen compounds of arsenic and antimony, care must be taken to add as little nitric acid as possible to the hydrochloric acid used in dissolving the sulphides of the metals, since the presence

even of moderate quantities of this acid, greatly interferes with the free disengagement of the gases. If there be *tin* with the arsenic and antimony, the metal will be deposited upon the plates of zinc used in evolving the hydrogen, from which it may be mechanically detached, dissolved in hydrochloric acid, and tested by the usual process.

(5.) *Meyer's method* (Liebig's 'Annalen,' May, 1848).—This is founded on the insolubility of antimoniate of soda. The mixture of the two metals is deflagrated with three times its weight of nitrate and carbonate of soda, the fused mass is washed with cold water, which dissolves out the arsenic acid, which, after reduction by sulphurous acid, may be precipitated by sulphuretted hydrogen, and determined in the usual manner.

184. Tin.

This metal is weighed as *peroxide*: it has also been attempted to estimate it by a *normal solution of iodine*.

Quantitative estimation as Peroxide.—The compound under examination is evaporated nearly to dryness, at a boiling heat, with strong nitric acid, to ensure the whole of the metal being in the state of peroxide; if any hydrochloric acid be present, it must be completely decomposed and expelled. The peroxide of tin, which by the action of the nitric acid has become converted into the insoluble modification, is filtered, washed, ignited, and weighed. Its composition is—

One equivalent of Sn	59 . .	78·66
Two ditto of O	16 . .	21·34
One ditto of SnO_2 . . .	75 . .	100·00

Tin may also be precipitated from its acid solution, whether in the state of a protosalt, or of a persalt, by sulphuretted hydrogen; in the former case the resulting sulphide is brown, in the latter case it is yellow; the gas must be passed through the solution till it smells strongly of it, and a gentle heat must afterwards be applied, by which a small quantity of sulphide, which is dissolved in the saturated liquor, becomes again deposited; the sulphide of tin must not be weighed as such, but converted into peroxide, which may be done by heating it, first gently and then intensely, in a porcelain crucible, till all the sulphur is removed in the form of sulphurous acid, the expulsion of which is facilitated by adding a small fragment of

carbonate of ammonia. Rose recommends to convert the sulphide of tin into peroxide by nitric acid, observing that, when the quantity of sulphide is at all considerable, its conversion into peroxide takes place by heat alone with extreme slowness.

Volumetric estimation:—

(1.) *Gaultier de Claubry's method* ('Comptes Rendus,' July 13, 1846).—As a normal solution, he employs 1 gramme of *iodine* dissolved in a *décilitre* of alcohol, sp. gr. 0·932, and the solution of tin is prepared with 1 gramme of this metal dissolved in hydrochloric acid, and diluted with water freed from air, so as to form a litre. By means of a graduated pipette, a demi-décilitre of the tin solution is measured off, and the burette, divided into tenths of a cubic centimètre, is filled with the normal solution; the latter is poured into the first, until it is no longer decolorized; half a décilitre of the tin solution, containing 5 décigrammes of tin, decolorizes 100°, or 10 cubic centimètres of the normal solution. If the tin ore under examination is soluble in hydrochloric acid, the operation is perfectly simple; if it does not dissolve in it, it is acted on with aqua-regia, containing much hydrochloric acid; and, when the tin is become converted into perchloride, an excess of hydrochloric acid is added, and it is then boiled with some *iron*, by which it becomes reduced to protochloride; the process is now conducted in the same manner as in the preceding case. If it happen to be an alloy containing only twenty per cent. of lead, hydrochloric acid will dissolve it; beyond that, however, only imperfectly; but, as aqua-regia scarcely acts on the compounds of lead, the alloy must be dissolved in nitric acid, evaporated to expel the excess of acid, and then treated with hydrochloric acid and iron. *Stannic acid*, especially when it has not been dissolved, is readily converted into protochloride, in the presence of an excess of hydrochloric acid and protochloride of iron, so that the assay is brought to the same state as when the product could be acted upon immediately with hydrochloric acid. When the compound to be analysed contains *arsenic*, *antimony*, *bismuth*, *copper*, or *lead*, the iron precipitates it, and again reduces the assay to the state of a tin solution. To precipitate the whole of the copper, and not to leave any of the protochloride of that metal in solution, a considerable excess of hydrochloric acid must be employed, and the boiling with iron continued for some length of time. The analysis of a salt of tin can be made with the same ease, and

if a mixture of a per- and proto-salt is examined, or any of the corresponding *haloid* compounds, the relative proportions can be determined by analysing the substance itself, and then making a second analysis of the product boiled with hydrochloric acid and iron. *Zinc* and *iron* do not interfere with the analysis by iodine, while the protosalts of iron and the corresponding haloid compounds decolorize the sulphate of indigo, which M. Pelouze had attempted to employ for the estimation of tin, and renders this process impracticable.

Iodine may, according to the author, be used to determine the quantity of tin in a solution containing various metals; but if there be present an *arsenite*, *sulphite* or *hyposulphite*, *phosphite* or *hypophosphite*, the normal solution will be decolorized as with protochloride of tin. It will be requisite, therefore, to oxidize these salts by nitric acid or by chlorine, and to reduce the tin to protochloride by means of iron.

(2.) *M. Stromeyer's method.*—He introduces the solution of protochloride of tin into an excess of sesquichloride of iron. The salt of iron becomes reduced to a minimum according to the following equation:—

$$SnCl + Fe_2\,Cl_3 = SnCl_2 + 2\,FeCl.$$

It is then estimated by a standard solution of permanganate of potassa, as if it were a salt of protoxide of iron. The results are accurate, but the method is only applicable in the absence of *copper* and *iron*, as these two metals decompose permanganate of potassa as well as of *tin*.

Separation of Protoxide of Tin from Peroxide of Tin.—Rose's method is the following:—The solution is divided into two portions; in one, the amount of the metal is determined by precipitating it by sulphuretted hydrogen, and then converting it into peroxide in the manner described above; the other portion is dropped into solution of chloride of mercury, and the subchloride of mercury precipitated, is filtered, washed, dried at a gentle heat, and weighed. From this weight, it is easy to calculate how much protoxide or protochloride of tin was contained in the solution, since the quantity of chlorine contained in the subchloride of mercury is the same as that contained in the protochloride of tin, by which it was precipitated; or, on the other hand, the quantity of chlorine in the subchloride of mercury is equivalent to the quantity of oxygen in the protoxide of tin, which acted as a precipitant.

Analysis of Alloys of Tin and Copper.—The process of M.

Cottereau ('Comptes Rendus,' June 29, 1846) is founded on the principle that copper is precipitated from its solutions by *zinc* before *tin*. The alloy is reduced to a fine powder, a certain quantity weighed off, and digested with boiling hydrochloric acid. Into the resulting solution of the protochlorides of copper and tin, a plate of zinc is introduced. By a previous assay of the copper contained in the alloy by the cuprometric process of M. Pelouze (p. 379), the quantity of copper is determined, and consequently an equivalent amount of zinc may be added to the solution; or the plate of zinc may be immediately introduced into the solution, and left there until a bright iron blade does not acquire a red tint on being immersed in the liquor. The strip of zinc is then removed, and the precipitate collected on a filter. Whichever plan be adopted, the filtered liquor is acted on just as if it were pure protochloride of tin. The protochloride of zinc formed does not in the least interfere with the reaction.

Separation of Tin from Antimony.—This is attended with difficulty. The following methods have been proposed:—

(1.) *Berthier's method.*—The two metals being dissolved in concentrated hydrochloric acid, tartaric acid is added to the solution, which is then diluted with water, *sulphite of ammonia* added, and the whole boiled. The tin is precipitated while the antimony remains dissolved.

(2.) *Levol's process* (Ann. de Chim. et Phys., Jan. 1845).—The alloy being reduced to a thin plate, is heated with hydrochloric acid; after some minutes' boiling, a saturated aqueous solution of chlorate of potassa is added in small quantities at a time, until the alloy entirely disappears. The two metals are then thrown down together by means of a bar of distilled zinc; the precipitate is removed from the zinc with the greatest care, a quantity of concentrated hydrochloric acid, about equal to what was employed at first, is added, and the whole is boiled so as to redissolve the tin without previously removing the chloride of zinc; when the action has terminated, that is, when nothing remains but the antimony, which is always the case after an hour's boiling, this metal then forms a very fine blackish powder: it is collected on a weighed filter, and the tin may now be immediately obtained from the liquors by sulphuretted hydrogen.

According to L. Elsner (Journ. für Prakt. Chem., vol. xxxv. p. 313), the above process has no claim to accuracy.

He found, on repeating the experiment with a mixture of $7\frac{1}{2}$ grains of tin and as much antimony, exactly according to the directions given by Levol, that the acid liquid filtered from the black powder, on being treated with sulphuretted hydrogen, yielded a precipitate which consisted evidently of two differently-coloured layers; the inferior layer was clearly the orange-red precipitate of sulphide of antimony, above which was the chocolate-brown protosulphide of tin. It is certain, therefore, that some antimony had dissolved with the tin. Elsner convinced himself that antimony is partly dissolved on being boiled with hydrochloric acid, and that consequently no quantitative method of separating it from tin can be founded on its insolubility in that acid.

(3.) *Rose's method* (Chem. Gaz., vol. v. p. 313).—Strong nitric acid is cautiously poured upon the metals, and when the violent oxidation has ceased, the whole is evaporated at a gentle heat, and the dry powder of the oxides fused in a silver crucible over an argand lamp, with an excess of hydrate of soda. The fused mass is softened with a large quantity of water, gently warmed, and the antimoniate of soda allowed to subside. When perfectly cold, the clear solution is passed through a filter: if this is done while it is still warm, the solution will contain some antimoniate of soda. The insoluble salt is again treated once or twice with water, allowed to settle and cool, and the liquid, when perfectly clear, passed through the filter. When the whole of the stannate of soda has been dissolved in this manner, the liquid which has been warmed with the antimoniate of soda remains opalescent; it must not be poured on the filter, as it would pass through turbid. A small quantity of a dilute solution of carbonate of soda may be added to it, which renders it clear; but the edulcoration must not be continued for any length of time, as otherwise some antimoniate would be dissolved.

The moist antimoniate of soda is now treated in a beaker with a mixture of hydrochloric and tartaric acids, in which it readily dissolves; and the filter, upon which mere traces of the salt should have collected, is washed with the same mixture. The antimony is then precipitated from the solution by sulphuretted hydrogen, and the amount of antimony estimated from the quantity of sulphide obtained. Rose reduces the sulphide of antimony by hydrogen in a porcelain crucible, through the lid of which a thin porcelain tube passes. A gentle heat is care-

fully applied, until the crucible no longer decreases in weight. After the reduction, the inner side of the lid is coated with metallic antimony, which, however, in no way interferes with the accuracy of the experiment.

The solution of stannate of soda is acidified with hydrochloric acid. It is not necessary to add so much acid that the whole of the eliminated oxide of tin is again redissolved. It is merely necessary that the solution should strongly redden blue litmus-paper. Upon this, sulphuretted hydrogen is passed into it. The sulphide of tin is converted by roasting into oxide. When it has been dried, it frequently decrepitates, by which, if care be not taken, a very considerable loss may be occasioned. It is, on this account, preferable to place it with the filter, while still moist, in a porcelain crucible, and to heat it for a long time very gently, and with access of air, in order to expel the sulphur at the lowest possible temperature. If a strong heat be given at the commencement, white fumes of oxide escape, especially when the air has free access. The higher sulphide of tin has the property of subliming somewhat, at certain temperatures; the vapours are oxidized by contact with the air, and form oxide of tin. This is also the cause of a white sediment of oxide of tin being formed upon the charcoal, when sulphide of tin is heated on charcoal before the blowpipe. A strong heat should not be applied until there is no longer any perceptible odour of sulphurous acid. After being strongly ignited, a piece of carbonate of ammonia is placed in the crucible, and, after its volatilization, a strong heat applied, with access of air, in order to expel the whole of the sulphuric acid formed; a small decrease of weight will be perceived.

The oxide of tin thus obtained never appears perfectly white; and the sulphide of tin, precipitated by sulphuretted hydrogen, does not possess a purely yellow colour, which Rose attributes to melting the metallic oxides with hydrate of soda in the silver crucible, traces of oxide of silver being removed by the alkaline solution. The results do not attain the highest degree of accuracy. Stannate of soda containing an excess of hydrate of soda does not become turbid by boiling, as stated by Fremy, and the solution may even be evaporated until crystals separate, which, on the addition of water, entirely dissolve, yet the antimoniate of soda contains a small quantity of oxide of tin; consequently the sulphide precipitated by sulphuretted hydrogen from the acid solution of the antimoniate

of soda contains a small amount of sulphide of tin, which does not part with the whole of its sulphur at the temperature at which the sulphide of antimony is reduced by hydrogen. For this reason a somewhat smaller amount of tin, a larger quantity of antimony, and a slight excess, is found in the analysis.

(4.) *Tookey's method* (Quart. Journ. Chem Soc., vol. xv. p. 464).—The author finds the process of reduction by metallic iron to answer perfectly. The hydrochloric solution of the two metals is digested at a gentle heat, with pure thin sheet iron, until the whole of the iron is dissolved; a considerable quantity of cold water is then added, the antimony is collected on a weighed filter, washed and dried; it should then be purified from traces of iron by digesting with cold dilute hydrochloric acid, dried in the water-oven, and weighed in the form of a grey powder. The tin is precipitated from the filtrate by sulphuretted hydrogen, the protosulphide of tin dried, and converted into binoxide by careful ignition.

Separation of Tin, Antimony, and Lead (Tookey).—When the ordinary method of separation was used, viz. oxidation by nitric acid, evaporation at a steam temperature, and extraction with water, the author found that it was impossible thoroughly to remove the lead; varying portions in different trials being retained in an insoluble state by the oxides of tin and antimony, probably in the form of antimoniate of lead. He therefore availed himself of the volatility of the chlorides of tin and antimony, and the fixity of chloride of lead to effect a separation; for this purpose about 10 grains of the alloy are introduced into a bulb expanded in the middle of a piece of hard combustion tube, having ingress and egress tubes bent at angles of 45 degrees, but in opposite directions; one pointing upwards, for introducing the alloy, and the other downwards, for collecting the volatile products in water: sufficient nitric acid having been poured on the alloy, the funnel tube is closed with a cork, and the oxidation effected at a moderate temperature. When it is converted into a perfectly white mass, the excess of acid is expelled by causing a gentle current of air to traverse the apparatus, a moderate heat being at the same time applied. A current of dry hydrochloric acid gas generated from fused chloride of sodium and sulphuric acid, is then transmitted slowly through the tube, the downward egress-end being immersed in a small quantity of water. When the mass becomes liquid from the absorption of gas, a gentle

heat is applied, the chlorides of tin and antimony distil over, and are condensed in the water, chloride of lead remaining. When the distillation is nearly finished, a greater heat is applied to expel the last traces of bichloride of tin, and lastly the chloride of lead, now perfectly free from tin and antimony, is heated to fusion, it is then removed from the tube and converted into sulphate, in which state it is weighed; the water containing the mixed chlorides of tin and antimony, after the addition of a little more hydrochloric acid, is digested with pure metallic iron until the whole of the iron is dissolved; cold water is then added: the precipitated antimony is then collected on a weighed filter, washed with cold water, and dried at 212°. The filtrate from the antimony is saturated with sulphuretted hydrogen; sulphide of tin is precipitated, which is converted into binoxide by ignition.

Separation of Tin and Arsenic; Analysis of Arsenates of Tin.—The mixed oxides, in a finely pulverized state, are placed in a small porcelain tray, and heated in a combustion-tube in a current of dry sulphuretted hydrogen; both oxides are reduced to sulphides, the sulphide of arsenic volatilizes completely, leaving sulphide of tin, which is first roasted, and then strongly calcined in a platinum crucible, it is hereby converted into stannic acid, in which state it is weighed.

Separation of Antimony, Tin, and Arsenic (Poggendorff's 'Annalen,' lxxvii. p. 110).—The mixture of stannate and antimoniate of soda, obtained by acting on the alloy with nitric acid, and subsequently fusing with hydrate of soda, is first washed thoroughly out of the crucible with water, and the insoluble antimoniate of soda allowed to separate. The solution which contains all the stannate of soda is now mixed with so much alcohol (specific gravity, 0·83), that its volume relatively to that of the water is as 1 to 3. In this spirituous solution the stannate of soda is completely soluble, while the last portions of antimoniate of soda are completely separated. The clear liquid having been filtered off, the antimoniate of soda is washed with stronger alcohol till some of the filtered liquid, rendered acid with a little dilute sulphuric acid, gives no longer a precipitate with sulphuretted hydrogen. The solution is heated to expel the alcohol, diluted with water, supersaturated with sulphuric acid, precipitated with sulphuretted hydrogen, and the sulphide of tin converted into oxide. The antimoniate of soda is dissolved in a mixture of hydrochloric

and tartaric acids, from which solution the antimony is precipitated by sulphuretted hydrogen. When arsenic is present in the alloy it is found in the solution containing the stannate of soda; this solution is supersaturated at once with hydrochloric acid, without previously driving off the alcohol, and sulphuretted hydrogen passed through it without previously separating the precipitated arsenate of tin. The whole is set aside till it scarcely smells of sulphuretted hydrogen, and the precipitate is collected on a weighed filter. The filtered liquid is heated for some time, by which any portion of sulphuretted hydrogen still present, and the greater portion of the alcohol, are expelled. It is then mixed with a solution of sulphurous acid, and again treated with sulphuretted hydrogen, when generally a further small quantity of sulphide of arsenic is precipitated. This treatment with sulphurous acid is not, however, necessary, if sulphuretted hydrogen is again passed immediately through the liquid separated from the sulphides. The small amount of sulphide of arsenic which is precipitated in this case is always free from every trace of sulphide of tin, and is kept separate, and only added to the sulphide of arsenic obtained in the separation of the arsenic and tin. These two metals contained in the precipitate by sulphuretted hydrogen are separated by being heated in a current of sulphuretted hydrogen, when the sulphide of arsenic is volatilized. The residual sulphide of tin is converted into oxide, and the sublimed sulphide of arsenic into arsenic acid. This method proved on examination to be absolutely accurate.

185. Platinum.

In whatever form this metal may be precipitated, it is invariably weighed in the reguline state. It may be precipitated from its solution as *ammonio-chloride of platinum*, as *potassio-chloride of platinum*, and as *sulphide of platinum*.

(1.) *Precipitation as Ammonio-chloride of Platinum.*—The acid solution is concentrated; it is then mixed with a concentrated solution of chloride of ammonium, and a sufficient quantity of spirits of wine added to effect the complete precipitation of the double salt: the precipitate is allowed to subside perfectly; it is then collected on a filter, and washed with spirits of wine till the fluid passes through quite colourless; it is dried, and ignited, by which it is completely decomposed, metallic platinum, in the form of a grey spongy powder, remain-

ing in the crucible. The ignition requires to be performed with great care: the dried double salt is transferred, filter and all, into a weighed platinum crucible, and is heated gently, the cover of the crucible being laid loosely on, as long as fumes of sal-ammoniac are seen to escape; the cover is then removed, and a stronger heat applied till the organic matter of the filter is consumed; the crucible is finally exposed to an intense heat. The reason why a gentle heat must be applied at first, is because a portion of the undecomposed double salt might otherwise be carried off with the fumes of the sal-ammoniac.

(2.) *Precipitation as Potassio-chloride of Platinum.*—The solution is mixed with chloride of potassium in excess, and alcohol added; the precipitated double salt is collected on a filter, dried at 212°, and weighed. It would not be safe, however, to estimate the platinum from the weight of the double salt, and, indeed, after ignition, it is not completely decomposed into metallic platinum and chloride of potassium; where accuracy is required, therefore, a known portion of the double salt dried at 212° must be introduced into a weighed bulbed tube, and heated to redness, while a stream of dry hydrogen gas passes through it. It thus becomes completely reduced, hydrochloric gas being evolved; when this has ceased, which is known by white fumes ceasing to be formed on bringing a glass rod or a feather dipped in ammonia-water near the end of the tube, the apparatus is allowed to cool, the chloride of potassium is then dissolved out with water, and the reduced platinum well washed. It is then again heated to low redness in a stream of hydrogen gas, and weighed; the weight obtained calculated upon the whole precipitate on the filter, gives the result.

(3.) *Precipitation as Sulphide.*—This is sometimes practised to separate platinum from such metals as are not precipitated from their acid solutions by sulphuretted hydrogen, as well as from others whose sulphides are insoluble in alkaline sulphides; in the former case, the gas is passed into the acid solution. No precipitation frequently takes place till heat is applied, when the solution turns brown, and sulphide of platinum is precipitated; it is not weighed as such, but after being washed, is ignited, by which it becomes reduced, and is then estimated in its metallic state: in the latter case, the solution is rendered neither neutral or alkaline, and sulphide of ammonium added in excess, in which the sulphide of platinum dissolves.

Separation of Platinum from Antimony, Arsenic, and Tin.—

This is readily effected by taking advantage of the volatility of the chlorides of the three last metals; all four are first precipitated together by sulphuretted hydrogen; the mixed sulphides are introduced into a bulbed tube, and heated in a stream of chlorine gas; platinum alone remains.

Analysis of Platinum ores (MM. Deville and H. Debray, 'Annales de Chimie et de Physique').—The following substances are contained in the ores of this valuable metal:—1, *Sand;* 2, *Osmide of Iridium;* 3, *Platinum*, *Iridium*, *Rhodium* and *Palladium* (probably an alloy); 4, *Copper* and *Iron;* 5, *Gold*, and a *little Silver*.

(1.) *Determination of the Sand.*—This is effected by heating a known weight (about 2 grammes) of the ore with five or six times its weight of pure granulated silver in a crucible, the sides of which have been previously glazed by melting borax in it; over the metals, 10 grammes of fused borax, and one or two pieces of wood-charcoal are placed, the heat is raised a little above the melting-point of silver, at which it is kept for some time; the vitreous matters are dissolved by the borax, and all the metals are contained in the button of silver which is found at the bottom of the crucible when cold; it is heated to faint redness and weighed, the weight subtracted from the sum of the weights of the ore and silver employed, gives the amount of sand.

(2.) *Determination of Osmium and Iridium.*—About 2 grammes of the ore are repeatedly treated with aqua-regia until the whole of the platinum is dissolved, which is known by the solution being no longer coloured. The insoluble residue is *osmide of iridium* in the form of spangles, together with the sand; it is washed by decantation, dried and weighed; by subtracting the weight of the sand obtained in the former operation, we get the weight of the osmide of iridium.

(3.) *Determination of the Platinum and Iridium.*—The solution obtained in the last operation is evaporated to dryness on the water-bath, redissolved in a little water, alcohol added, and then crystals of sal-ammoniac in great excess; after standing for twenty-four hours the orange-yellow or reddish-brown precipitate is thrown on filter, and washed with alcohol, it consists of the ammonio-chlorides of platinum and iridium, but a portion still remains in the solution; the double chlorides of the two metals, after being dried, are heated to low redness in a platinum crucible, and the filter is burnt at the lowest

possible temperature; to favour the reduction of the iridium, and the escape of the last traces of osmium, a piece of paper saturated with turpentine is introduced into the crucible. The heat is now raised gradually to whiteness, and the reduction of the metal is finished in a current of hydrogen. The filtrate from the double chlorides of platinum and iridium is concentrated until the greater part of the sal-ammoniac crystallizes out; it is then allowed to cool, upon which a deep violet-coloured precipitate is formed; this is ammonio-chloride of iridium, mixed with a little of the corresponding platinum salt; it is collected on a filter, and washed first with a solution of sal-ammoniac, and then with alcohol, after which it is dried and ignited in a current of hydrogen. The results of the two reductions are weighed and digested at about 120° F., with repeated portions of aqua-regia diluted with five or six times its bulk of water, till the liquid is no longer coloured: all the *platinum* is dissolved, leaving as a residue *iridium* in a state of purity.

(4.) *Determination of the Palladium, Iron, and Copper.*—These metals are contained in the liquor from which the platinum and iridium have been separated. The alcohol and chloride of ammonium are evaporated off, the removal of the latter being facilitated by the addition of nitric acid, which transforms it into nitrogen and hydrochloric acid; the evaporation is continued almost to dryness; the residue is transferred to a weighed porcelain crucible, and when dry, is moistened with sulphide of ammonium, and loosely covered with two or three grammes of pure sulphur. The crucible is covered, placed in a larger clay crucible, and surrounded with pieces of wood charcoal, a cover is then put upon the clay crucible, and it is brought slowly up to a bright-red heat, the fire being lighted at the top of the furnace in order to avoid the projection of any matter from the crucible, which might happen if it were too quickly heated. When cold, the inner crucible contains *palladium* in the metallic state, with the sulphides of *iron* and *copper*, and also the *gold* and the *rhodium*. The mixture is digested for a long time at 150° with concentrated nitric acid, which dissolves the *palladium*, *iron*, and *copper*, converting them into nitrates. These are dissolved out by water, and the residue well washed; the solution and washings are evaporated to dryness and then calcined at a strong red-heat; the *palladium* is reduced, and the *iron* and *copper* are converted into oxides, which are easily separated from the palladium by strong hydrochloric acid,

and the latter, now in a state of purity, is strongly ignited and weighed. The chlorides of copper and iron are treated in the usual way for the determination of each metal.

(5.) *Determination of the Gold.*—This metal is contained in the residue (4.) insoluble in nitric acid: it is weighed and then treated with dilute aqua-regia, which dissolves the *gold,* and sometimes, but rarely, a trace of *platinum,* the presence of which is detected by chloride of ammonium; the difference between the weight of the crucible before, and after, the treatment by aqua-regia gives the weight of the gold.

(6.) The residue left in the crucible is *rhodium,* which is reduced in a current of hydrogen and then weighed.

The authors caution experimenters to beware of the ill effects of osmium, which particularly attacks the eyes; and also to avoid breathing the vapour from the aqua-regia.

186. Gold.

This metal, like the preceding, is always weighed in the metallic state, in which it is precipitated from its solutions by *protosulphate of iron,* or by *oxalic acid.* A method of estimating the metal indirectly by means of standard solutions has also been published by O. Henry. Gold may also be precipitated from its acid solution, by sulphuretted hydrogen. The sulphide is readily reduced by heat alone.

Precipitation by Protosulphate of Iron.—If the solution contain nitric acid, it must be evaporated nearly to dryness, with the addition of successive portions of hydrochloric acid, the residue is dissolved in water, acidulated with hydrochloric acid, and mixed with an excess of a clear solution of protosulphate of iron. It is set aside for some time in a warm place, till the reduced gold has completely subsided in the form of a fine brown powder, which is then filtered, gently ignited, and weighed. The object in expelling the nitric acid, is to prevent the formation of aqua-regia, which might redissolve a portion of the precipitated gold. Solution of *protonitrate of mercury* may be employed in the place of protosulphate of iron; the latter, however, is preferable as the reducing agent.

(2.) *Reduction by Oxalic Acid.*—In certain cases it is not convenient to introduce another metal into the solution from which gold is to be precipitated; *oxalic acid* is then employed as the reducing agent. The solution as before, is freed from nitric acid, and oxalate of ammonia added; if the solution

does not already contain free hydrochloric acid, a quantity is next added, and the mixture set aside in a warm place; the whole of the gold is deposited in the form of yellow scales, which are collected on a filter, washed, gently ignited, and weighed. In cases where gold is the only fixed substance present, its quantity may be estimated by simply evaporating the solution to dryness and igniting the residue, and, when in combination with other substances which are incapable of being precipitated from acid solutions by sulphuretted hydrogen, gold may be separated by that reagent, and the resulting sulphide decomposed by ignition in a platinum crucible.

The rationale of the reduction of terchloride of gold by protosulphate of iron is this:—

$$AuCl_3+6FeO,SO_3=2(Fe_2O_3,3SO_3)+Fe_2Cl_3+Au.$$

The rationale of the reduction by oxalic acid is as follows:—

$$AuCl_3+3(HO,C_2O_3)=Au+3HCl+6CO_2.$$

Estimation of Gold by standard solutions (Henry, Journ. de Pharm., Jan. 1847).—This process, which was devised by the author in consequence of the difficulty which he experienced in appreciating very minute quantities of gold, either by weighing, or by cupellation, in certain investigations in which he was engaged relative to the new processes of gilding and silvering of Elkington and Ruolz, is founded on the principle, that in a mixture of terchloride of gold, a basic salt, and copper, a quantity of the latter metal, equivalent to that of the gold, separated either in powder, or upon the object to be gilt, is dissolved. When the amount of gold upon a gilt object, or in a bath which has been, or is to be employed in gilding has to be ascertained, the following plan may be adopted. The objects, weighed with care, are digested with hot pure nitric acid; as soon as the copper forming the basis is dissolved, the solution is diluted with distilled water, and the gold is soon seen to settle at the bottom of the vessel in small brilliant scales. These are collected, and, after washing, dissolved in aqua-regia; the solution is evaporated with great precaution nearly to dryness, so as to obtain a ruby-red product, soluble in water; this is terchloride of gold with a little acid. This product is now dissolved in distilled water, and mixed with five or six times its weight of pure bicarbonate of potassa or soda, dissolved in distilled water; the mixture is heated, conveyed into a ground stoppered flask, and a somewhat large amount of finely divided copper, which has been previously

heated in a current of hydrogen, added to it; the mixture is now and then shaken, and after about an hour the liquid assayed. A very minute quantity of the liquid is poured upon a watch glass and treated with protosulphate of iron; if the liquid does not yield a black or grey precipitate, it is a sign that it contains no gold in solution; should the contrary occur, more copper must be added, and the liquid again agitated. When the whole of the gold has been precipitated upon the copper, the liquid is carefully saturated with pure sulphuric acid so as to be *slightly acid.* By this means all the copper precipitated in the state of *carbonate* is dissolved, without the gold or *metallic copper* being at all acted upon. It is filtered, and a solution of pure *ferrocyanide of potassium* of known strength carefully added by means of a graduated burette, until a precipitate ceases to be formed; the number of divisions of the instrument employed to precipitate the copper is noted, and in this manner the quantity of the metal dissolved in the liquid is ascertained.

When it is a solution which is to be, or has been, used for gilding, the author advises to precipitate the diluted acid solution by a current of sulphuretted hydrogen, to collect the precipitate and strongly calcine it after washing. The sulphide of gold being reduced to the metallic state, the calcined residue is redissolved in nitric acid, and the gold which has remained unattacked, dissolved in aqua-regia, and treated as above described.

The use of the ferrocyanide of potassium, to determine the amount of copper which represents the gold in a compound, is founded on the fact, that this reagent is still very sensitive when sulphide of sodium has no longer any perceptible action. The conditions requisite for the success of the operation are:— 1st, to take care that the copper employed is perfectly *free* from oxide; 2nd, to be certain that, after contact with the copper, no gold remains in solution; 3rd, to saturate the mixture exactly with pure sulphuric acid after the reaction; 4th, to mix as quickly as possible, at a gentle heat, the copper and the bicarbonate with the solution of the terchloride of gold; 5th, to add the test liquid, which has been made shortly before use, with precaution, and only by drops, when but a slight chestnut or dark-red precipitate is produced.

M. Henry quotes a number of experiments, the results of which prove the exactness of the process, as well as the ease and quickness with which it may be performed.

Separation of Gold from Platinum.—The alloy is boiled in aqua-regia, and the gold reduced by oxalic acid; from the filtered solution the platinum may be thrown down in the metallic state by *formic acid;* or the platinum may first be precipitated from the hydrochloric solution by chloride of potassium, and the gold in the filtrate may then be reduced by protosulphate of iron.

Separation of Gold from Antimony, Tin, and Arsenic.—This may be effected in the same manner as the separation of platinum from these metals, viz. by heating the mixed sulphides in a stream of chlorine gas. The chlorides of tin, antimony, and arsenic distil over, while the gold remains behind. Elsner employs metallic zinc as the precipitant for gold, which he finds to remove the metal from a solution of its chloride more effectually than protosulphate of iron. For the quantitative determination of gold, however, in a mixture of platinum, gold, and tin, he prefers protosulphate of iron, on account of the greater simplicity of the operation. He first precipitates the platinum by a concentrated solution of chloride of ammonium, and afterwards the gold from the filtrate by a recently-prepared solution of protosulphate of iron. He found that when an excess of this reagent was employed, the filtrate from the precipitate still gave a beautiful dark-red colouring with protochloride of tin, though no precipitate was observed.

Analysis of alloys of Gold.—Several methods are employed. In the first place, an approximation to the relative proportions of the constituents is obtained by the touchstone and the assay-needle; the former is a black and polished basalt; black flint and pottery will serve the same purpose. The assay-needles are small fillets of gold, alloyed with different and known quantities of silver or copper: the sets may consist of pure gold; pure gold $23\frac{1}{2}$ carats, with half a carat of silver;* 23 carats of gold, with one carat of silver; $22\frac{1}{2}$ carats of gold, with $1\frac{1}{2}$ carat of silver, and so on till the silver amounts to four carats, after which the additions may proceed by whole carats. Other needles may be made in the same manner, with copper instead

* In estimating or expressing the fineness of gold, the whole mass spoken of is supposed to weigh twenty-four carats of twelve grains each, either real, or merely proportional, like the assayers' weights; and the pure gold is called fine. Thus, if gold is said to be twenty-three carats fine, it is to be understood that, in a mass weighing twenty-four carats, the quantity of pure gold amounts to twenty-three carats.

of silver, and other sets may have the addition, either of equal parts silver and copper, or of such proportions as the occasions of business may require. When a specimen of gold is about to be examined, it is rubbed on the touchstone, and the colour which it leaves is compared with that communicated to the stone by the assay-needles taken successively; that which leaves a mark most nearly resembling that produced by the specimen, is in composition most nearly allied to it, and, as the composition of the needle is known, so the operator is enabled to judge of the quantity of silver necessary to be added for the *quartation* proof. The alloy is next cut into small thin plates, and fused in the cupel (see SILVER), with 3½ times as much pure silver as it contains gold, and with three or four times its weight of lead. After the operation, the gold and the silver remain, the oxide of copper being absorbed with the oxide of lead by the cupel. This process is termed *quartation*, because the gold forms one-fourth part of the cupelled alloy, a proportion which admits of the complete subsequent extraction of the silver by the action of nitric acid. The alloy of gold and silver is next reduced to thin plates, weighed, and gently heated with nitric acid, diluted, and quite free from nitrous and hydrochloric acids; the silver dissolves, the gold remaining untouched. The acid being saturated, a stronger acid is added, and the solution is gradually brought to boil, by which the perfect separation of the silver is accomplished, the gold retaining still the form of the original plate. It is therefore easily weighed; previous to which, however, it must be washed with distilled water, as long as any traces of silver appear, by the test of common salt, and then heated to redness. The loss which the mass experiences by the process of cupellation, indicates the quantity of copper contained in the alloy, and the proportion of silver is afterwards found by the action of the nitric acid. It must particularly be borne in mind, that if the nitric acid be not free from nitrous acid, and especially from hydrochloric acid, a portion of the gold, sufficient to affect seriously the result of the assay, may be dissolved.

Mr. Makin has drawn attention to the loss which occurs in parting operations, and refining on a large scale, from the solution of gold in nitric acid, even when quite free from hydrochloric acid, in consequence of the formation of nitrous acid. When the silver is present in large quantity, the solvent action appears to be restrained by electrical action; but as the

silver is removed, the solution of the gold goes on more rapidly. The cause of the evolution of nitrous acid is evident as long as there is any silver present, and it often results from the use of charcoal, to prevent "bumping." When charcoal is thoroughly carbonized, it does not materially affect the acid, but if it contain woody matter, nitrous acid is sure to be set free.

Purification of Gold by Cementation.—The alloy is reduced to a thin plate, and surrounded in a crucible with a pulverulent mixture of four parts of brick-dust, one of calcined vitriol, and one of common salt. It is then exposed for 16 or 18 hours to a strong red-heat. The vapours of hydrochloric and sulphuric acids which are formed, attack the metals mixed with the gold, and the mass is prevented from fusing by the brick-dust. If the first cementation has not been found sufficient to purify the gold, the operation is repeated, but, in the place of common salt, nitre is used. The same method is employed to refine the surface of gold articles after they are polished. The cementation here produces the same effect as tartar and salt, in which silver goods are boiled to give them a white colour.

Purification by Fusion with Sulphide of Antimony.— Some borax is fused in a crucible, so that the walls become lined with the vitrified flux; a mixture of two parts of sulphide of antimony and one of the gold to be assayed is then introduced. The sulphur combines with the foreign metals, and the antimony unites with the gold; the alloy being removed, the scoriæ are a second time fused, with the addition of two parts more of sulphide of antimony, and, when the whole of the gold is extracted, the various alloys are mixed together and heated in an open vessel, with two parts of sulphur. The sulphide of antimony volatilizes, leaving the gold; to increase the action, a current of air from a pair of bellows may be directed on the surface of the melted mass, or, what is perhaps still better, the mixture of the two metals may be fused in a large crucible, with three times its weight of nitre, by which the antimony becomes oxidized and dispersed, the gold remaining untouched. Another method is to fuse the gold alloy with a mixture of *oxide of lead* and *sulphur*, and to add to the fused mass charcoal in the state of fine powder; the gold is thus obtained alloyed with the lead only, from which it may be separated by cupellation.

In this operation it frequently happens that some of the antimony remains alloyed with the gold, a plan for removing

which has been suggested by Mr. Warrington (Jour. Chem. Soc., vol. xiii. p. 33). It consists in employing about ten per cent. of oxide of copper, and a small quantity of borax, with which the alloyed gold must be kept in a well-fused state for half an hour. The result is a perfectly malleable gold, containing a small percentage of copper and well fitted for the purpose of coinage.

187. Selenium.

When existing in solution in the form of *selenious acid*, it is reduced by sulphite of ammonia, which separates selenium in the form of a cinnabar-red powder, which, if boiled, becomes black; it is collected on a filter, and dried at a very gentle heat: nitric acid, if present in the solution, must be decomposed and expelled by hydrochloric acid, previous to the addition of the sulphite of ammonia. When, however, selenium is contained in a solution, as *selenic acid*, it must first be reduced to selenious acid by boiling with hydrochloric acid, and then precipitated by sulphite of ammonia.

As selenium is precipitated from its solution when in the form of selenious acid by sulphuretted hydrogen, it may thus be separated from all those substances which are not precipitated by that reagent. *Selenic acid* does not, however, possess the property of being precipitated by sulphuretted hydrogen; when selenium, therefore, exists in this state, and has to be separated from other substances, it must be reduced to selenious acid.

Sulphide of selenium has the following composition:—

One equivalent of Se	39·75	55·40
Two ditto of S	32·00	44·60
One ditto of SeS	71·75	100·00

According to Oppenheim, selenium may be estimated by fusing the body containing it with cyanide of potassium, dissolving the fused mass in water, and then supersaturating the solution with hydrochloric acid, which effects the complete separation of the selenium at the end of a few hours. The fusion ought to be performed in an atmosphere of hydrogen; it is advisable when the substance contains free selenious acid, previously to saturate this acid with an alkaline carbonate, so as to avoid volatilizing small portions before the cyanide of potassium has had time to react upon it. The solution obtained by treating the fused mass with water, contains seleno-cyanide

of potassium, together with a small quantity of selenide. It is necessary on this account to boil the liquid for some time before the addition of hydrochloric acid, to convert the selenide into seleno-cyanide. Without this precaution, a portion of the selenium might be disengaged in the form of seleniuretted hydrogen.

The ordinary process for estimating selenic acid consists in precipitating it as a baryta salt. According to Rose, however (Poggendorff's 'Annalen der Physik und Chemie,' cxiii. 472 and 624), seleniate of baryta is much more soluble than sulphate, and it possesses in a high degree the property of carrying down the soluble salts which are contained in the liquid; it is always better, therefore, to reduce the selenic acid to selenious acid by hydrochloric acid, and then to precipitate the selenium with sulphurous acid.

Selenium cannot be separated from the metals with which it is combined when the sulphides of these metals are insoluble in sulphide of ammonium, by making use of the solubility of selenium in this reagent, because the insoluble metallic sulphide is almost always mixed with selenium. Most frequently selenium may be separated from metals by heating the mixture in a current of chlorine; the chlorides of selenium are sufficiently volatile to render the separation generally easy. In acid solutions of the selenites of metals not precipitable by sulphuretted hydrogen, the selenium may be precipitated by this gas in the state of sulphide.

To estimate the alkalies and alkaline earths combined with selenium, it is sufficient to fuse them with chloride of ammonium. The alkali or alkaline earth remains in the state of chloride; one single fusion, or two at the most, are sufficient to drive off all the selenium.

When it is desired to estimate the selenic acid in an insoluble combination, particularly in seleniate of baryta, the compound is decomposed by an alkaline carbonate, the transformation into alkaline seleniate takes place even in the cold; it is then easy to reduce the selenic into selenious acid by means of hydrochloric acid.

Analysis of Seleniate of Lead.—It is reduced to a fine state of division, and diffused in water, through which a current of sulphuretted hydrogen is passed; the liquor filtered from the sulphide of lead is boiled, to expel the excess of sulphuretted hydrogen, and the selenic acid is precipitated as seleniate of

baryta, which is decomposed by an alkaline carbonate as above directed.

188. Tellurium.

According to Rose (Poggendorff's 'Annalen,' vol. cxii. p. 307), the best reagent to precipitate tellurium from solutions of tellurous acid is sulphurous acid. The solution should be strongly acidulated with hydrochloric acid. Phosphorous acid may also be used, but not so effectively. To analyse compounds of telluric acid, Rose directs to fuse the compound at a gentle heat with cyanide of potassium in a long-necked flask through which a current of hydrogen is passed. After fusing for about ten minutes, it is allowed to cool in the current of hydrogen; the flask is then filled up with water, and turned upside down in a beaker filled with the same fluid. The *telluride* of potassium dissolves, colouring the water red; it decomposes in the air, depositing tellurium; this decomposition is hastened by passing a current of air through the solution. The deposited tellurium is collected on a filter, and the liquid after the addition of hydrochloric acid is treated with sulphurous acid to reduce a small quantity of tellurous acid which may have been formed. A boiling solution of cyanide of potassium dissolves very little tellurium, *telluro-cyanide of potassium* is formed in this case; from this solution, tellurium is precipitated by hydrochloric acid. The results obtained by fusing *tellurates* with alkaline carbonates are less accurate than when cyanide of potassium is used.

Estimation as Sulphide.—Tellurous acid is completely precipitated from its hydrochloric solution by sulphuretted hydrogen; it may be dried at 212°, and weighed as sulphide, the composition of which is—

One equivalent of Te . . .	64·5 . .	66·84
Two ditto of S . . .	32·0 . .	33·16
One ditto of TeS . .	96·5 . .	100·00

Tellurous acid may also be estimated by simple evaporation on the water-bath; when it is dissolved in other acids, especially in nitric acid, the dry mass is heated in a platinum crucible at not too great a heat. If there be hydrochloric acid in the solution nitric acid must be added.

Tellurium, like *Selenium*, cannot be separated from other metals by sulphide of ammonium, because a portion of tellurium invariably remains in the precipitated sulphides.

Separation of Tellurium from Selenium.—The substance is fused with ten times its weight of cyanide of potassium in an atmosphere of hydrogen, in which the fused mass is allowed to cool. This is dissolved in abundance of water, and a current of atmospheric air passed through the solution. At the expiration of twelve hours the deposited tellurium is separated by filtration, and the selenium is estimated in the liquid in the manner already described.

Separation of Selenium, Tellurium, and Sulphur.—The substance is fused with cyanide of potassium in an atmosphere of hydrogen, the fused mass is dissolved in water, and the tellurium precipitated by a current of air; the filtered liquid is boiled, the selenium is precipitated with hydrochloric acid, and the sulphur in the filtrate is changed into sulphuric acid by the action of chlorine, after supersaturating with potassa.

189. Tungsten.

The method proposed by Berzelius for quantitatively estimating tungstic acid, was to precipitate it from its neutral or alkaline solution in the form of sulphide of tungsten by sulphide of ammonium, and then to add excess of the reagent, by which the sulphide is dissolved; from this solution it is reprecipitated by nitric acid, and having been washed and dried, it is roasted by a gentle heat, whereby it becomes converted into tungstic acid, in which state it is weighed. The composition of tungstic acid is—

One equivalent of W (Wolfram)	92	79·31
Three ditto of O	24	20·69
One ditto of WO_3	116	100·00

A method of determining the quantity of tungstic acid in neutral salts by nitrate of mercury, has also been described by Berzelius.

The following is the plan proposed by M. Marguerite ('Comptes Rendus,' Feb. 3rd, 1845). He recommends it as being very simple and perfectly exact.

The salt to be analysed is placed in a small platinum crucible, and several times its weight of pure concentrated sulphuric acid added. At first a gentle heat is employed, and then the temperature is gradually raised to a red-heat. After calcination the residue is composed of an acid sulphate and of free tungstic acid. It is thrown on a filter, washed with water, charged with

sal-ammoniac, which prevents the tungstic acid from combining with water, and from passing through the filter, which frequently happens, even when it has been ignited. When the last washings no longer precipitate chloride of barium, the residue is ignited to drive away the sal-ammoniac, and a few drops of nitric acid added to obviate any error that might arise from a slight reduction which the tungstic acid may have undergone, and to ensure the perfect combustion of the last traces of charcoal of the filter. In this way the tungstic acid may be directly determined.

Analysis of Insoluble Tungstates.—They are fused with carbonate of potassa in a platinum crucible, by which operation tungstate of potassa is formed, which salt, being soluble in water, may be treated with sulphide of ammonium as above directed.

Analysis of Wolfram.—This mineral, which is a double tungstate of iron and manganese, is best analysed according to Wöhler, by mixing it in a finely divided state with two parts of dry chloride of calcium, and fusing in a platinum crucible. The melted mass is treated with water, which dissolves out the chlorides of manganese and iron, and leaves the tungsten in the form of insoluble tungstate of lime.

Another method (Wöhler).—The levigated mineral is digested with a mixture of four parts of concentrated hydrochloric acid, and one part of nitric acid, until it is completely decomposed, the solution is then evaporated to dryness on the water-bath, the chloride of manganese and sesquichloride of iron are dissolved out, the tungstic acid filtered off, washed with alcohol, dissolved in ammonia, again filtered, the solution evaporated, the residual ammonia-salt ignited with access of air, and the tungstic acid weighed; the filtrate containing alcohol is evaporated to expel the latter, diluted with water, and the oxides of manganese and iron separated in the usual manner.

190. Molybdenum.

This metal is weighed in the form of the grey bisulphide. It is precipitated from its solution in sulphide of ammonium by hydrochloric or acetic acid. The compound thus precipitated is the tersulphide, which may indeed be converted by ignition into molybdic acid (MO_3), but it would not be safe to estimate the metal in this form, because, at the temperature necessary

to decompose the tersulphide, a portion of molybdic acid would be volatilized. Rose, therefore, directs the precipitate occasioned by adding hydrochloric or acetic acid to the solution of tersulphide of molybdenum in sulphide of ammonium, to be gently ignited in a small weighed retort, by which it loses one of its atoms of sulphur, leaving the bisulphide, which has the following composition:—

One equivalent of Mo	. . . .	48	. . 60
Two ditto of S	. . . . .	32	. . 40
One ditto of MoS_2	. . .	80	. . 100

From all the metallic oxides, the sulphides corresponding to which are not soluble in sulphide of ammonium, *molybdenum*, like *tungsten*, may be separated by that reagent. For this purpose, the compound is dissolved in excess of hydrochloric acid; should *lead* or *silver* be present, the chlorides thus formed are removed by filtration, excess of sulphide of ammonium containing excess of sulphur is added, and the mixture digested for an hour. It is then filtered, the filtrate containing the tersulphide of molybdenum is supersaturated and digested with acetic or hydrochloric acid, and the precipitate treated as above directed.

Analysis of Molybdate of Lead (Wöhler).—The finely powdered mineral is completely decomposed by digestion with nitric acid, the solution is neutralized with ammonia, and digested with excess of sulphide of ammonium. The sulphide of lead which is thus formed is filtered off from the dissolved molybdate, washed with dilute sulphide of ammonium, dried at 212°, and weighed. From the solution, the sulphide of molybdenum is precipitated by dilute nitric acid, collected upon a filter, washed, dried at 212°, and weighed. A weighed portion of it is then introduced into a bulb-tube, and heated in a stream of hydrogen until it loses no more sulphur; from the weight of residual bisulphide calculated for the total amount of the precipitate, that of the molybdic acid is ascertained.

191. Titanium.

This metal when it exists in solution in the form of titanic acid may be completely precipitated by ammonia, taking care not to use a large excess of the precipitant; it shrinks very much in drying. When ignited it has a light brown tinge; its composition is—

One equivalent of Titanium	. 25	. .	60·97
Two ditto of Oxygen	. 16	. .	39·03
One ditto of TiO_2 . .	41	. .	100·00

Acid solutions of titanic acid are precipitated by long continued boiling, but the precipitation is not complete, unless it exist in solution in sulphuric acid. The precipitated titanic acid must be washed with acidulated water, but as this always dissolves a little titanic acid, it cannot be completely separated from other substances in this way. If pure water be employed to wash the precipitated titanic acid, it gradually carries the whole of it through the filter. Titanic acid after ignition is insoluble in all acids but concentrated and boiling sulphuric. When fused with pure or carbonated alkalies, it enters into combination with them. The fused mass loses a portion of its alkali by washing with water, and an acid titanate of the alkali is left which is soluble in warm hydrochloric acid. When the solution is diluted and boiled for a long time, nearly the whole of the titanic acid is separated in the form of a heavy white precipitate. If a piece of zinc, iron, or tin be introduced into the hydrochloric solution of an alkaline titanate, the liquor assumes a blue colour, and a blue precipitate is formed which gradually becomes white; a similar precipitate is formed on adding excess of potassa or ammonia to the hydrochloric solution, having previously removed the zinc, tin, or iron. When titanic acid or titanates of bases which do not impart colours to fluxes are heated in contact with a fragment of pure tin, or still better of pure zinc, with microcosmic salt in the inner blowpipe flame, a blue or violet-coloured bead is produced which disappears in the outer flame; by this reaction, titanic acid is well distinguished from all other substances.

Estimation of Titanic Acid in Silicates.—Titanic acid exists in many silicates in which its presence may easily be overlooked. Scheerer ('Annalen der Chemie und Pharmacie,' Band cxi. 372) gives the following method for separating and estimating it:—When the silicate is decomposed in the ordinary way by acids or by carbonate of soda, the greater part of the titanic acid is found in the precipitate obtained by adding ammonia to the solution filtered from the silicic acid; but some remains with the latter. To separate this it is heated with hydrofluoric and sulphuric acids, and the residuum is added to the precipitate which has been previously ignited. The united mass in which besides

titanic acid, alumina, oxide of iron, manganese, and some lime and magnesia may be present, is fused with bisulphate of potassa, the temperature being gradually raised, until the greater part of the sulphuric acid in excess, is dissipated. The fused mass is then dissolved in a large quantity of water, and sulphuretted hydrogen is passed through until the peroxide of iron is reduced to protoxide; after this, the solution is boiled, and the fluid being kept hot, carbonic acid is passed through; the bases remain in solution, while the titanic acid is precipitated.

Separation of Titanic Acid from the metals of the Fifth Group.—This is easily effected by sulphuretted hydrogen, which in an acid solution, does not precipitate titanic acid, whilst all the oxides comprised in this group are thrown down by this reagent as sulphides.

Separation of Titanic Acid from Oxide of Iron.—Rose directs to add to the solution containing these two oxides, first, pure tartaric acid in excess, and afterwards ammonia, and then to precipitate the iron as sulphide, by sulphide of ammonium. If no other fixed substance besides titanic acid be present in the filtrate from the sulphide of iron, it may be evaporated to dryness and ignited till all the volatile substances, and the carbon of the tartaric acid have been burnt off; titanic acid remains. Mosander places the finely divided compound in a porcelain tube, and ignites it in a current of dry hydrogen gas, until the oxide of iron is completely reduced, which is known by aqueous vapour ceasing to be condensed in a glass tube connected with the porcelain tube in which the ignition has taken place. The residuum is allowed to cool in the stream of hydrogen; it is then weighed, and digested in strong hydrochloric acid which dissolves the iron and leaves the titanic acid.

To determine the titanium which frequently exists in pig-iron, Riley (Journ. Chem. Soc., vol. xvi. p. 391) proceeds in the following manner:—200 grains of the pig are dissolved in dilute hydrochloric acid; when nearly the whole is dissolved, and the action of the acid has ceased, more hydrochloric acid is added, and the solution boiled, so as thoroughly to extract the iron. The solution is then thrown on dried counterpoised filters encircling each other, and the residue on the filters well washed to remove all the iron. It is then treated with a dilute solution of caustic potassa, washed once, and then again treated with the alkali so as entirely to remove the silica. The potassa is thoroughly washed out, and the filters washed, first with hydrochloric acid, and then

with boiling water; it is then dried at 250° until the weight is constant. This gives the graphite, on burning which, a residue of a dirty light-brown colour is left. This is fused with bisulphate of potassa; the fused mass is dissolved in cold water and then boiled for some hours; on standing, the titanic acid subsides, it is collected on a filter, washed with dilute hydrochloric acid, dried, ignited, and weighed.

II. ACIDS.

192. Acids of Sulphur.

(1.) *Sulphuric Acid.*—This acid is nearly always estimated by converting it into *sulphate of baryta.* If the substance to be examined be dissolved in water, it must be acidified with pure hydrochloric acid, heated nearly to ebullition, and chloride of barium or nitrate of baryta added till no further precipitation occurs. The sulphate of baryta formed, usually subsides quickly and completely, but it should be allowed to settle thoroughly before it is filtered; it is washed on the filter repeatedly with boiling distilled water, dried, and ignited, the weight of the ash left by the filter, which has been determined by a previous experiment, being deducted: for the composition of sulphate of baryta, see p. 277. If the substance analysed be dissolved in nitric acid, it must be well diluted with distilled water before it is precipitated by a baryta salt, otherwise nitrate of baryta may be thrown down, which would afterwards require long-continued washing to remove; in all cases, the operator must be careful to wash the precipitate on the filter till the washings no longer give any cloudiness when dropped into dilute sulphuric acid. Should the substance under examination be insoluble in water and in hydrochloric acid (sulphates of baryta, strontia, lime, or lead, for example), it must be fused in a platinum crucible (porcelain in the case of lead) with about four times its weight of a mixture of pure carbonate of soda and carbonate of potassa, the whole having been previously well mixed by trituration in a mortar; the mass should be kept in a state of fusion for some time, to ensure complete decomposition, and when cool, transferred to a dish, and digested with distilled water repeatedly, till all the soluble matter is removed; this contains the whole of the sulphuric acid of the compound analysed, in combination with soda and potassa, together with the excess of the alkaline carbonates; the base or bases with which

the acid had been previously in combination, remain in the form of insoluble carbonates, and are to be determined in the manner directed in the preceding pages. The sulphuric acid is precipitated from the solution by nitrate of baryta or chloride of barium, the liquid having been previously supersaturated with hydrochloric acid, or with nitric acid, if lead be present; the precipitant in that case being nitrate of baryta.

Volumetric estimation of Sulphuric Acid (Schwartz).—A standard solution of nitrate of lead is prepared, containing 33·100 grammes in each litre, which solution corresponds to the standard solution of bichromate of potassa employed by the author for the volumetric estimation of lead (see LEAD). This lead solution is added to the fluid containing the sulphuric acid in such proportion as to allow a slight excess of the lead, after which, the precipitate is filtered and washed, and the filtrate being mixed with acetate of soda, the excess of lead is estimated by the standard solution of bichromate. Every cubic centimètre of the lead solution requires 0·008 grammes of sulphuric acid for precipitation; should the base (as in sulphate of lime) occasion some inconvenience, it may be removed by boiling with carbonate of soda; and hydrochloric acid, if present, must be expelled, by adding nitric acid and evaporating to dryness. Phosphoric and arsenic acids also occasion embarrassment, as in the presence of acetate of soda, tribasic phosphate and arsenate of lead are both thrown down; this method of estimating sulphuric acid would seem therefore to have somewhat limited applications.

(2.) *Sulphurous Acid.*—The precipitate which this acid forms with barytic salts is soluble in hydrochloric acid, by which it is at once distinguished from sulphate of baryta; when a soluble sulphite, or a salt of any of the other lower acids of sulphur is presented for analysis, it is converted into sulphate by careful and protracted digestion with nitric acid, or with aqua-regia: dry *sulphites*, *hyposulphites*, and *hyposulphates* may also be converted into sulphates by fuming nitric acid. When a mixture of a sulphate and a sulphite has to be examined, two different portions of the compound are analysed; in one the quantity of *sulphuric* acid is determined in the ordinary manner, namely, by precipitating it from its hydrochloric solution by chloride of barium or nitrate of baryta; the other portion is digested with nitric acid or with aqua-regia, and, the sulphite being thus converted into sulphate, the solution is also precipi-

tated by a barytic salt. The difference in the two quantities of sulphuric acid found, furnishes the data for calculating the proportion of *sulphite* in the compound. The same method may be adopted for analysing mixtures of sulphates with salts of any of the other lower acids of sulphur.

*Analysis of a mixture of the different compounds of Sulphur with Oxygen** (Fordos and Gelis).—The process is founded on the different action which chlorine and iodine exert on the acids of sulphur. Thus, neither of these bodies exerts any action on sulphuric or hyposulphuric acids, while they rapidly convert sulphurous into sulphuric acid. On passing a current of chlorine into a dilute solution of a hyposulphite, sulphur is precipitated, and sulphurous acid disengaged; and on passing the gas into a solution of the sulphyposulphuric acid of Langlois, or the bisulphyposulphuric acid of Fordos and Gelis, the whole of the sulphur becomes converted into sulphuric acid; again, iodine, though without any action on the sulphohyposulphates, exerts an action of a peculiar nature on solutions of the hyposulphites. MM. Fordos and Gelis apply these facts to the analysis of mixtures of salts of the different acids of sulphur. Thus, suppose the solution to contain a sulphate, a sulphite, a hyposulphite, a hyposulphate, and a bisulphohyposulphate. The liquid is divided into four equal portions.

I. The sulphuric acid is determined by chloride of barium, the precipitated sulphate of baryta being washed first for some time with boiling distilled water, and then with water rendered slightly acid with hydrochloric acid; the solution must not be acid previous to adding the chloride of barium, or a partial oxidation of the sulphurous acid may take place, thus occasioning too large an amount of sulphate of baryta.

II. Another portion is mixed with a considerable quantity

* Six of these compounds have been well made out, and the existence of several others is probable; the six well-defined acids have the following composition:—SO_3, SO_2, S_2O_2, S_2O_5, S_3O_5, S_4O_5, and they have been thus classified by Berzelius:—

Monothionic SO_3, SO_2. Sulphuric and sulphurous acids.
Dithionic . . S_2O_3, S_2O_5 Hyposulphurous and hyposulphuric acids.
Trithionic . S_3O_5 . . Sulphyposulphuric acid of Langlois.
Tetrathionic . S_4O_5 . . Bisulpho-hyposulphuric acid of Fordos and Gelis.

Besides these, a new series of acids of sulphur has been announced by Plessy ('Comptes Rendus,' Aug. 1845), to which he assigns the following composition:—S_5O_6, S_5O_7, S_6O_7, S_8O_{10}; and M. Wackenroder, and MM. Fordos and Gelis, have each described an acid having the composition S_5O_5.

of carbonate of magnesia, and saturated with iodine, the quantity required being carefully noted; the amount of sulphuric acid contained in the liquid is again determined by chloride of barium; the quantity of sulphate of baryta obtained will be greater than in the first experiment, and the increase will indicate the quantity of sulphurous acid, and the weight of iodine which it was necessary to employ in order to convert it into sulphuric acid; when this point is attained, it is easy, without having recourse to any other experiment, and by a simple subtraction, to procure all the elements necessary for the determination of the amount of hyposulphurous acid. The quantity of iodine which had been required to convert the sulphurous acid into sulphuric, is subtracted from the total amount employed; the difference will have been absorbed by the hyposulphurous acid; *two* equivalents of this acid absorb *one* of iodine. In treating the liquid with iodine, an alcoholic solution of known strength is employed, or small fragments of iodine are added by degrees to the liquid from a flask, the weight of which has been previously determined. The solution is very rapid, and the point of saturation is easily ascertained. As soon as the liquor acquires a yellow colour, no more should be added. The change of colour is very striking, and it is quite useless to add starch or any other foreign body to the solution. The necessity of adding carbonate of magnesia to the liquid previous to the addition of the iodine, arises from the fact, that water is decomposed by the *sulphite*, which is also in solution; it becomes sulphate, taking oxygen from the water; at the same time the iodine takes the hydrogen, and hydriodic acid is formed; but this acid would, if at the moment of its production it did not find a base to saturate it, act on the undecomposed portion of the sulphite, or on the hyposulphite, which the liquid likewise contains, and there would be a loss of sulphurous acid and a deposit of sulphur.

III. This portion of the liquid is employed to determine the amount of bisulpho-hyposulphuric acid. It is saturated with iodine, without, however, keeping any account of the quantity employed. The iodine forms as before, a sulphate at the expense of the sulphite, and a bisulpho-hyposulphate at the expense of the hyposulphite. This quantity will go to increase that already contained in the solution. This being done, about 100 parts of water are added to the liquid under examination, through which a current of chlorine is then passed. This gas will bring to the state of sulphate, the whole

of the sulphur of the bisulpho-hyposulphate, without attacking that of the ordinary hyposulphite. When the saturation is complete, chloride of barium is added to the solution; the weight of the sulphate of baryta obtained will represent the sulphur of the sulphate, of the sulphite, of the hyposulphite, and of the bisulpho-hyposulphite. As the operations made with the first and second portions of the liquid will have indicated the quantity of sulphur contained in the three first, the difference between the two weights will serve to determine the amount of sulphur contained in the latter, and consequently its entire amount.

IV. There will now only remain the hyposulphuric acid. To determine this it will suffice to know the total amount of sulphur in the mixture analysed; for then, after having assigned to the four other acids the amount pertaining to them, the difference must of course belong to the hyposulphuric acid. The solution is evaporated to dryness, a small quantity of caustic soda being added, to retain the sulphurous gases; the solid residue is treated in the usual manner with fuming nitric acid, and the amount of sulphur determined by chloride of barium.

(3.) *Hydrosulphuric Acid* (Sulphuretted Hydrogen):—

I. *Estimation of, in a free state, by a Solution of Iodine in Iodide of Potassium.*—This method is based on the fact that one equivalent of iodine decomposes one equivalent of hydrosulphuric acid, the results being hydriodic acid and sulphur:—

$$HS + I = HI + S.$$

5 grammes of pure iodine (perfectly dry) are dissolved in a concentrated solution of pure iodide of potassium, and water added till the whole occupies exactly *one litre*=1000 cubic centimètres; each cubic centimètre containing therefore 0·005 gramme of iodine. A known quantity of the sulphuretted water to be tested is diluted with distilled water that has been boiled, and cooled out of contact with air, some thin starch paste is mixed with it, and the ioduretted iodide dropped in from a burette until a permanent blue colour is obtained; now, as one equivalent of iodine=127, corresponds to one equivalent of sulphuretted hydrogen=17, the quantity of iodine contained in 1000 cubic centimètres of the standard solution of 5 grammes, is equivalent to 0·669 gramme of sulphuretted hydrogen, hence the calculation is easily made. This method was first proposed by Dupasquier. In the analysis of sulphuretted mineral waters, Fresenius recommends that the iodine solution should

be diluted five times, that is, until each cubic centimètre contains 0·001 gramme of iodine.

The presence of *hyposulphites* renders this process inexact, as the iodine is changed into hydriodic acid by hyposulphurous acid as well as by sulphuretted hydrogen. Lyte ('Comptes Rendus,' Oct. 20, 1856) proposes to precipitate the sulphur as sulphide of silver by means of the double hyposulphite of silver and soda dissolved in excess of hyposulphite of soda. This reagent is prepared by dissolving chloride of silver in a solution of hyposulphite of soda: it may be kept for a long time, especially with the addition of one or two drops of ammonia. The sulphuretted hydrogen contained in a mineral water, may be removed by passing a current of pure hydrogen gas through it, and receiving the removed gas in a solution of acetate of lead; sulphide of lead is precipitated, which is converted into sulphate, from the amount of which, that of the sulphuretted hydrogen is calculated.

II. *As Sulphide of Arsenic.*—If the acid be in solution in water, as, for example, in certain mineral springs, the water is mixed with a clear solution of arsenious acid in hydrochloric acid, and the precipitate which forms allowed to subside; it is then collected on a filter, washed with cold water, dried at 212°, and weighed: for the composition of sulphide of arsenic, see page 407. If the hydrosulphuric acid be evolved in the gaseous form, the substance from which it is expelled is heated in a flask, and the gas received into a vessel containing a solution of arsenious acid in caustic potassa: the last traces of the gas are removed from the flask by pouring into it, solution of bicarbonate of potassa. The operation being completed, the alkaline ley is supersaturated with hydrochloric acid, and the sulphide of arsenic thereby precipitated, collected, dried, and weighed.

Separation of Sulphur from the Alkalies and Alkaline Earths.—If the compound be soluble in water, its solution may be mixed with a solution of *chloride of copper*, upon which sulphide of the latter metal is precipitated. The precipitate is collected on a filter as quickly as possible, to prevent the oxidation of a portion of the sulphide, and then treated with red fuming nitric acid, by which the sulphur is brought into the state of sulphuric acid, and may then be precipitated with the proper precautions, by a soluble salt of baryta. The weight of the sulphate of baryta obtained furnishes data for calculating

the amount of sulphur present in the substance analysed. If the sulphide to be examined be not readily soluble in water, it may be decomposed in a flask by dilute sulphuric or hydrochloric acid, the hydrosulphuric acid evolved being conducted through a series of Wolfe's bottles, about two-thirds filled with a neutral solution of chloride of copper; three bottles may be employed, the latter containing, in addition to the metallic chloride, a little caustic ammonia, to ensure the complete absorption of the hydrosulphuric acid gas. The gas remaining in the flask at the end of the operation must be driven forward into the bottles, by a current of carbonic acid gas. This is effected by pouring into the flask through its funnel, a solution of carbonate of ammonia, not, however, sufficient to neutralize the acid, because it may happen that a portion of sulphur has been deposited in the generating flask during the decomposition, which it would of course be necessary to collect on a tared filter, wash, dry, and weigh; but if the liquor were rendered alkaline (supposing the sulphide of an alkaline earth to have been under examination), an insoluble carbonate would be precipitated, which would render the collection of the sulphur difficult.

The following method for the prompt estimation of the soluble sulphides contained in crude sodas, has been proposed by Lestelle ('Comptes Rendus'). It is based on the insolubility of sulphide of silver, and the solubility of all other argentiferous salts, in the presence of ammonia. A standard solution of ammonio-nitrate of silver is prepared by dissolving 27·69 grammes of silver in pure nitric acid, adding 250 cubic centimètres of ammonia, and then diluting with water to the volume 1 litre = 1000 cubic centimètres; each cubic centimetre of this solution corresponds to 0·010 gramme of monosulphide of sodium. The substance to be analysed having been dissolved in water, ammonia is added, and it is then boiled. The ammoniacal silver liquid is then added, drop by drop, by means of a burette divided into tenths of a cubic centimètre. A black precipitate of sulphide of silver takes place. When nearly all the sulphur is precipitated, the liquor is filtered, and a fresh quantity of the silver solution is poured in, until after repeated filtrations, a drop of this liquid produces only a slight opacity. The estimation is then at an end, and it is only necessary to read the divisions indicated by the burette, and to compare this number with that of the weight. To estimate very small

quantities of sulphide, the argentiferous liquid must be more diluted, so that each cubic centimètre corresponds to 0·005 gramme of sulphide.

Analysis of Compounds of Sulphur with Bases.—Sulphur is readily detected in sulphides and in sulphates by fusing the sample with soda upon charcoal before the blowpipe; a hepar is thus obtained, which, on being moistened, is easily recognized by means of silver; as, however, it may still be uncertain whether the sulphur existed in the compound in the form of a sulphate or of a sulphide, Von Kobell has suggested the following simple method of solving the question:—The finely pulverized sample is boiled with caustic potassa in a porcelain crucible, and heated till the potassa begins to melt; or the sample is fused with hydrate of potassa in a platinum spoon before the blowpipe. The mass is then dissolved in a little water, and filtered; a bright strip of silver is placed in the solution; and, if the sample contain a sulphide, the hepatic reaction is frequently immediately perceptible, but sometimes only after a few hours. With very small quantities, the platinum spoon, with the flux, may be placed in a small glass with some water, and the silver introduced. The silver is easily restored to brightness by rubbing it with leather and a little caustic lime: sulphates after such treatment have no reaction on the silver.

Nitro-prusside of Sodium as a Test for Sulphur.—Any substance containing sulphur, when heated with carbonate of soda, either with or without the addition of carbonaceous matter, according as a deoxidizing action is, or is not required, will yield an alkaline sulphide. On adding to the fused mass a drop of the solution of nitro-prusside of sodium, a magnificent purple colour is produced. This test is so delicate that, according to Bailey ('Silliman's Journal,' May, 1851), the presence of sulphur may be detected in the smallest particles of coagulated albumen, horn, nails, feathers, mustard seed, etc., which can be conveniently supported on a platinum wire for blowpipe experiments. Dana ('Silliman's Journal,' Nov. 1851) gives the following more minute directions for the use of this elegant test:—Heat by the blowpipe, any sulphide or sulphate (or anything containing sulphur) upon charcoal, with carbonate of soda; put the fused mass into a watch-glass with a drop of water, and a particle not larger than a pin's head, of the nitro-prusside of sodium; there will be a magnificent purple

at once. When this test is tried on parings of nails, hair, albumen, etc., Dana advises that the carbonate of soda be mixed with a little starch, which appears to prevent the loss of any sulphur by oxidation. If a piece of hair four inches long be coiled round one point of a platinum support, moistened, dipped into a mixture of carbonate of soda with starch, and then heated by the blowpipe, the fused mass will give with the nitro-prusside the unmistakable reaction indicative of sulphur.

By this test the presence of sulphur in *hops*, *wines*, silk, etc., is easily detected. The substance under examination, is placed in a flask with a piece of sheet zinc, diluted hydrochloric acid is poured over it, and the gas conducted into the solution of nitro-prusside. If the gas contain but a minimum of sulphuretted hydrogen, the first bubble causes a violet cloud in the solution: after passing the gas for a short time it assumes the magnificent colour of the solution of permanganate of potassa. The vapour of hydrochloric acid passing over with the gas may be arrested by filtering it through cotton-wool, though it does not affect the reaction unless it be continued too long.

Metallic sulphides may be analysed in the dry way, by mixing them with thrice their weight of pure dry carbonate of soda, and an equal weight of nitre, to which must be added a considerable quantity of pure dry chloride of sodium. If the sulphide loses sulphur by heat, the mixture is kept for some time in fusion in a porcelain crucible; by this operation, the sulphur is separated from the metal with which it was originally combined, and is transferred in the form of sulphuric acid to the alkali; a soluble sulphate is thus produced, which may be precipitated by chloride of barium, and the quantity of sulphur calculated from the weight of sulphate of baryta formed. This process is applicable to the determination of sulphur in *coal* and *coke*. A quantity not exceeding 20 grains of the fuel is intimately mixed with 500 grains of a mixture of 4 parts of pure chloride of sodium, 2 parts of pure nitre, and 1 part of pure carbonate of soda, the mixture is gradually heated in a platinum dish till the whole is in tranquil fusion, and the heat is continued till all blackness has disappeared. When cold, the fused mass is washed out of the dish with boiling water into a beaker, the solution is supersaturated with pure hydrochloric acid, filtered (if necessary), and precipitated at a boiling heat by chloride of barium.

MM. Cloez and Guignet ('Comptes Rendus,' June 7th,

1858), suggest the employment of permanganate of potassa as an agent of oxidation for the determination of sulphur in sulphuretted compounds, and particularly in gunpowder. About one gramme of the material to be analysed, is put into a small matrass with a saturated solution of pure permanganate of potassa; and the liquid is boiled, with the addition of permanganate from time to time, until the mixture has a persistent violet tint; all the sulphur is hereby converted into sulphuric acid. The oxide of manganese which the liquid holds in suspension is dissolved by hydrochloric acid, the solution is concentrated, if necessary, by evaporation, a little nitric acid added, and then precipitated by chloride of barium.

Estimation of Sulphur in Iron and Copper Pyrites.—The following alkalimetrical method has been proposed by Pelouze (Ann. de Chim. et de Phys., 3rd series, vol. lxiii.). It is based upon the property which chlorate of potassa possesses in the presence of an alkaline carbonate, of transforming into sulphuric acid, the sulphur contained in metallic sulphides. The sulphuric acid formed neutralizes a portion of the alkaline carbonate, it is only necessary therefore to ascertain how much uncombined alkali exists in the mixture after fusion, to learn the quantity that has been saturated by the sulphuric acid formed from the sulphur of the sulphide, and this is done by a standard solution of sulphuric acid. The normal acid employed by Pelouze is of such a strength that 92·4 cubic centimètres are exactly neutralized by 10 grammes of pure and dry carbonate of soda; these numbers correspond to equal equivalents of carbonate of soda, and monohydrated sulphuric acid. A litre of normal acid contains 100 grammes of monohydrated acid, or 32·653 of sulphur. The process is conducted as follows:—1 gramme of the mineral is intimately mixed in a porcelain mortar with 5 grammes of pure and dry carbonate of soda, 7 grammes of chlorate of potassa, and 7 grammes of pure fused or decrepitated common salt, the mixture is heated to dull redness for eight or ten minutes in a platinum crucible. When nearly cold, the fused mass is washed into a beaker, boiled and filtered, the residue on the filter being well washed with boiling water. The filtrate and washings being well mixed, are now neutralized with the normal sulphuric acid. Example:—Suppose 34 cubic centimètres have been required, subtract this from 46·2 (the quantity that would have been required to neutralize 5 grammes of carbonate of soda), and there will remain 12·2 cubic centi-

mètres, which represent the sulphuric acid formed by the pyrites; this number multiplied by 32·653, and divided by 100, gives the weight of the sulphur sought, viz. ·0398, or 39·8 per cent. The process does not occupy more than thirty or forty minutes, and the errors involved in it, do not, according to the author, exceed 1½ per cent. of the weight of the sulphur to be determined.

Determination of Sulphur in Sulphide of Lead.—The sulphur is converted into sulphuric acid by digesting the ore in fuming nitric acid: the sulphate of lead produced is dissolved in hot caustic potassa, the alkaline solution is filtered from the insoluble matters, and the lead again precipitated as sulphide by sulphuretted hydrogen, it is received on a filter, washed, dried, and digested in a weighed platinum capsule with fuming red nitric acid; it is thus again converted into sulphate, in the form of which salt it is weighed.

Sulphide of silver and *sulphide of bismuth* must be decomposed by pure nitric acid; the substances should be reduced to as fine a state of division as possible, and projected into a flask capable of being closed with a stopper, and containing the very strongest fuming nitric acid; the bottle must be closed the moment the sulphide is introduced, and occasionally agitated; when the action slackens a gentle heat may be applied. In the case of *sulphide of silver*, should any of the sulphur have escaped oxidation, it may be dissolved by adding, in small portions, chlorate of potassa; but in the case of *sulphide of bismuth*, the unoxidized sulphur must be collected on a tared filter, washed with acetic acid, dried, and weighed; from the clear filtrate, the bismuth is precipitated by sulphuretted hydrogen, and from the filtrate from the precipitated sulphide of bismuth, the sulphuric acid is precipitated by a salt of baryta, hydrochloric acid having been previously added.

Separation of Sulphur from metals by Chlorine Gas.—This method is applicable to the analysis of compound sulphides of those metals, the chlorides of which are not volatile at a low red-heat. The substance is introduced into a bulbed tube connected with an apparatus by means of which a stream of dry chlorine gas may be passed through it. The disposition of the apparatus is seen in Fig. 76: *a* is the flask containing the materials for generating chlorine gas, which is dried by passing first through the Wolfe's bottle *b*, containing concentrated sulphuric acid, and then through the siphon-shaped tube *c*, containing

chloride of calcium; the sulphide to be analysed is weighed, and carefully introduced into the bulbed tube *d*, bent at a right angle, and dipping into water contained in the bottle *e*. If the

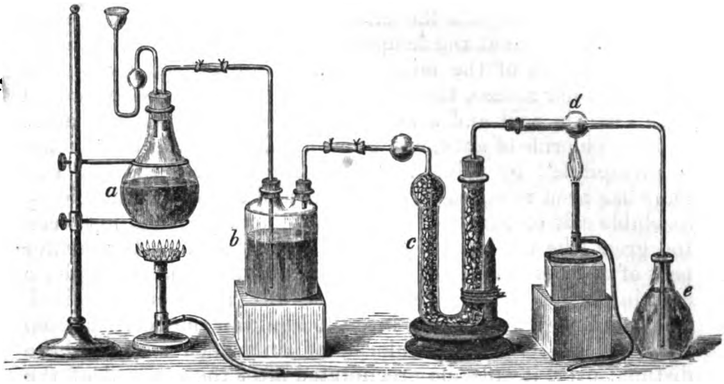


Fig. 76.

process cannot be conducted under a flue, it may be advisable to close the mouth of the bottle *e* with a cork, through which a tube is inserted, which may convey the excess of chlorine into another bottle, containing milk of lime, or potassa, thus preventing annoyance to the operator by the escape of the irritating gas into the apartment. The whole apparatus is first filled with chlorine, which is made evident by the yellow-green colour of the space above the water in the bottle *e*; a very gentle heat is then applied to the bulb, the sulphide is decomposed, its metallic base or bases combining with the chlorine, while the sulphur is driven forward into the bottle *e* in the form of ***chloride of sulphur***, which is immediately decomposed by the water into hyposulphurous acid, hydrochloric acid, and sulphur; the former, by the action of the chlorine, passes into sulphurous acid, and finally into sulphuric acid, so that the last result of decomposition is sulphuric acid, hydrochloric acid, and a greater or less quantity of free sulphur. When the action is over, the bulb is heated towards the bend, so as to force the whole of the chloride of sulphur into the bottle *e*; the tube is then cut off under the bend, and the separated end thrown into the bottle. The excess of chlorine is expelled from *e* by the application of a gentle heat, it is allowed to remain at rest for some hours till the sul-

phur has completely solidified, it is then collected on a tared filter, washed, dried, and weighed, and the sulphuric acid is lastly precipitated by nitrate of baryta or chloride of barium.

Rose applies the above method to the analysis of mixed sulphides of those metals the chlorides of which are either partly or wholly volatile at the temperature employed. For example, in the analysis of the mixed sulphides of *antimony*, *iron*, and *zinc;* in such a case, the water in the bottle *e* must be mixed with tartaric acid and a small quantity of hydrochloric acid; and the chloride of antimony which distils over into the bottle *e* is precipitated by sulphuretted hydrogen, after the free sulphur has been removed by filtration, and the sulphuric acid by a soluble salt of baryta. If the heat employed has not been too great, the whole of the chloride of zinc, and the greater part of the perchloride of iron, will be retained in the bulb; a certain portion of the latter, however, will have been volatilized, and will have found its way into the liquid in the bottle *e*, from which, together with any chloride of zinc which may also have distilled over, it must be precipitated after the removal of the antimony, by sulphide of ammonium.

Determination of Sulphur in Nitrogenous organic compounds (Fleitmann).—Sulphur exists in nitrogenous organic substances, such as caseine, albumen, and fibrine, in two different forms; one portion is removed by heating the substance in a concentrated solution of caustic potassa; the other portion remains combined with the organic substance. Fleitmann determines the amount of this combined sulphur, by first dissolving the compound in caustic potassa, and then digesting the solution for some hours, with frequent agitation, with a sufficient quantity of recently-precipitated hydrated oxide of bismuth; when cold, the liquid is supersaturated and digested for some time with excess of acetic acid; it is then filtered, and the washed sulphide of bismuth is oxidized with the filter in a silver crucible, by fusion with potassa and nitre, and the sulphur thus converted into sulphuric acid, is determined in the usual way as sulphate of baryta.

Estimation of Sulphur in volatile organic compounds (Debus, Liebig's 'Annalen,' Oct. 1850).—One equivalent of bichromate of potassa which has been purified by recrystallization, is dissolved with two equivalents of carbonate of potassa, or soda, in water, and the liquid evaporated to dryness; in this way, a lemon-coloured mass, consisting of one equivalent of neutral

chromate of potassa and half an equivalent of carbonate of potassa or soda, is obtained. It is powdered, and, in order to remove the last portions of water, exposed to a good red-heat in a Hessian crucible, and then filled while hot, into a glass tube sealed at one end and drawn out somewhat at the other, so that when wanted, the chromate of potassa can be conveniently poured into the combustion-tube without loss. This precaution is necessary with the use of carbonate of potassa, as it absorbs water from the air, and, on being subsequently heated in the combustion-tube, again parts with it, and cracks the tube. After the chromate of potassa has cooled in the above-mentioned corked glass tube, a layer of it of about three to four inches in length is poured into the combustion-tube, such as is used in organic analysis; the substance is then added, and then again a few inches of the mixture of chromate and carbonate of potassa. When the substance to be analysed is a solid, it is intimately mixed with the chromate of potassa in the combustion-tube, by means of a wire, twisted at one end like a corkscrew. When this is done, the empty portion of the combustion-tube is filled with a mixture of chromate and carbonate of potassa, placed in a furnace, and heated as for an organic analysis. When the whole is incandescent, oxygen is disengaged from a small retort, and passed in a slow current over the red-hot mixture for about half an hour or an hour. When cold, the tube is cleansed of adherent ash, and cut into several pieces over a sheet of paper; these are placed in a beaker, and so much water poured over them as may be necessary to dissolve the calcined mass. The liquid thus obtained is strongly acidified with hydrochloric acid, the chromic acid reduced with alcohol, and boiled till it becomes green. It is now filtered from the insoluble oxide of chromium, which is washed, first with water acidified with hydrochloric acid, afterwards with alcohol, and then dried. The filtered green liquid, which contains nearly the whole amount of sulphuric acid, is placed aside for a time, and the oxide of chromium (which always most tenaciously retains a small quantity, frequently one or two per cent., of sulphuric acid, in the form of a basic salt) is collected on a filter and dried. The oxide of chromium is then emptied into a platinum crucible, and the filter burnt. It is mixed with one part of chlorate and two of carbonate of potassa, and heated to redness until the whole of the oxide of chromium is converted into chromate of potassa. The fused mass is dis-

solved in dilute muriatic acid, the chromic acid reduced by alcohol, and the liquid added to that previously obtained. The united solutions are now heated to boiling, the sulphuric acid precipitated by chloride of barium, and the amount of sulphur calculated from the sulphate of baryta formed.

193. Acids of Phosphorus.

Phosphoric Acid.—In a solution which contains nothing but phosphoric acid, the amount of that acid may be estimated, by evaporating to dryness, with the addition of a known weight of recently ignited protoxide of lead; the residue after being heated to redness is weighed; the increase of weight indicates the amount of phosphoric acid. The presence of nitric acid does not interfere with the accuracy of this method.

The quantitative determination of phosphoric acid, when in combination with bases, and in the presence of other acids, is frequently attended with considerable difficulties, especially when it exists in small quantities only. The following are the principal methods at present in use.

(1.) *Estimation as Pyrophosphate of Magnesia. Applicable when the phosphoric acid is in combination with an alkali.*

Chloride of ammonium, ammonia, and sulphate of magnesia are added to the solution, which is then well agitated, or stirred with a feather; a glass rod should not be used for the purpose, as the crystalline double salt which is precipitated, adheres so firmly to those parts of the sides of the beaker which have been touched by the glass rod, that it cannot afterwards be readily removed. The mixture is allowed to remain at rest for several hours; it is then filtered, and the precipitate washed with water containing a little ammonia, in which it is almost insoluble; the washing must not be continued too long, but stopped immediately it is found that a few drops of the filtrate, when evaporated on platinum foil, leave no residue; it is then ignited, first gently, and afterwards strongly: for the composition of the ignited salt, see page 281. This method does not apply to the analysis of phosphates after they have been ignited, without a previous preparation, as has been shown by Weber (Chem. Gaz., vol. v. p. 450); the reason is, that they are converted by heat from tribasic into bibasic salts, and bibasic or pyrophosphoric acid forms with magnesia a salt which is much more soluble in water than tribasic or common phosphoric acid. By the action of acids it is true that pyrophosphoric acid is converted

into the tribasic acid, but Weber found that the transformation was not perfect, even when the compound was treated for a considerable time with concentrated sulphuric acid. In order to ascertain which of these two phosphoric acids we have under examination, the following test may be applied. The compound is dissolved in nitric acid, and precipitated by ammonia; the precipitate, after long standing, is collected on a filter; to the filtrate, nitrate of silver is added, and the ammoniacal liquid is then carefully neutralized with nitric acid; the appearance of a white turbidness, or the formation of white flakes, indicates the presence of pyrophosphoric acid. If the phosphoric be in combination with an alkali, it will, if the acid be tribasic, give a *yellow* precipitate with nitrate of silver (see p. 146). When the phosphoric acid in a phosphate is to be separated and determined by magnesia, and is not contained in the solution as the tribasic compound, the phosphate must be fused with excess of carbonate of soda. This can be done in all cases when the phosphoric acid is combined with the alkalies, or those metals which are completely decomposed by fusion with carbonate of soda; but it does not succeed in converting the phosphoric acid into the tribasic compound, when in combination with the alkaline earths, as these are only imperfectly decomposed. The only way to reprecipitate the pyrophosphate of magnesia from its solutions by ammonia, is to heat it for some time with concentrated sulphuric acid, when, on solution, it can be almost entirely precipitated by ammonia.

The precipitates which the tribasic and bibasic phosphoric acids produce with magnesia, differ essentially from each other in their external properties. The first is granular, crystalline, and soon subsides, especially when warmed; the latter is voluminous and flocculent, and remains long suspended in the liquid. Small quantities of pyrophosphoric acid cannot be separated, or even detected, by magnesia.

(2.) *Estimation by Nitrate of Silver* (Chancel).—This method is founded on the insolubility of the yellow phosphate of silver ($3AgO,PO_5$) in a neutral liquid. The weighed substance is dissolved in nitric acid; the solution is diluted with distilled water, and to the clear liquid is added, first a sufficient quantity of nitrate of silver, and then a slight excess of *carbonate of silver*. The saturation of the free nitric acid takes place rapidly, without the application of heat; in a few moments the yellow phosphate of silver is thrown down. When the super-

natant liquid no longer reddens litmus-paper, the precipitation is complete. The precipitate is collected on a filter and washed. When the washing is finished, the filter is perforated by a platinum wire, and the whole of the precipitate washed out into a flask, and dissolved in nitric acid. The silver is then precipitated by hydrochloric acid, and from the filtrate, the phosphoric acid is thrown down as ammonio-magnesian phosphate, by the addition of an ammoniacal solution of sulphate of magnesia.

(3.) *Estimation as Phosphate of Sesquioxide of Uranium.*—This method is well adapted for the separation of phosphoric acid from the alkaline earths, particularly *magnesia*, a separation usually attended with much difficulty. It does not succeed so well in the presence of *iron* and *alumina*, these substances being in part precipitated with the phosphate. To the solution of the phosphate in hydrochloric acid, or in water, nitrate of uranium is added; it is then supersaturated with ammonia, and afterwards acidified with acetic acid: phosphate of uranium is precipitated. The precipitation is known to be complete, by the supernatant fluid having a yellow tint: if incomplete, a fresh quantity of nitrate of uranium is added, and afterwards ammonia and acetic acid. The precipitate is allowed to deposit from the warm solution, and is washed several times by decantation with boiling water: the settling of the precipitate is favoured by the addition of chloride of ammonium. It is collected on a filter, washed with hot water containing chloride of ammonium, and dried: the dry precipitate is removed as completely as possible from the filter, calcined in a platinum crucible, the filter being burnt separately.

The composition of phosphate of sesquioxide of uranium is—

Two equivalents	of U_2O_3	. . . .	288·0	80·22
One ditto	of PO_5	. . . .	71·0	19·78
One ditto	of $2(U_2O_3)PO_5$	.	359·0	100·00

By the following modification, suggested by R. Arendt and W. Kopp (Chem. Centralb. 1857), phosphoric acid may be estimated by acetate of sesquioxide of uranium, in the presence of *iron*. The substance is dissolved in the smallest possible quantity of hydrochloric acid, and the sesquioxide of iron is reduced to protoxide, by means of *protochloride of uranium*. This salt is somewhat troublesome to prepare. The authors direct to dissolve ammonio-carbonate of uranium in double

the quantity of hydrochloric acid required to effect solution: to add a few drops of solution of bichloride of platinum, and to throw into the mixture some fine copper turnings. The mixture is boiled for ten or fifteen minutes, or until the liquid assumes a distinct green colour. To remove the subchloride of copper, the boiling is continued until water produces a copious precipitate in a sample of it. When this is attained, the whole is diluted with water and allowed to cool, it is then filtered, and sulphuretted hydrogen in excess is transmitted through the filtrate: the precipitated sulphide of copper is filtered off, a considerable quantity of chloride of ammonium is added, and the solution is boiled until every trace of sulphuretted hydrogen has disappeared. The solution of protochloride of uranium thus obtained is a powerful reducing agent. The protochloride of uranium thus prepared is added to the solution containing phosphoric acid and peroxide of iron, until a distinct green colour is produced, or until a drop of sulpho-cyanide of potassium does not produce a red colour. Ammonia is then added to alkaline reaction, then acetate of *sesquioxide* of uranium, and free acetic acid, together with a few drops of acetate of *protoxide* of uranium, (obtained by precipitating the protochloride with ammonia, and redissolving in warm acetic acid,) and the mixture is heated to boiling. The liquor must have a distinct greenish colour, not a dirty tinge, which shows the presence of undissolved protoxide of uranium. It is set aside till the precipitate has settled, the supernatant liquid is then decanted on a filter, the precipitate is boiled with water containing chloride of ammonium, and again decanted; this operation is repeated once or twice, and finally the precipitate is thrown on the filter, washed, dried, and ignited in the manner above directed.

(4.) *Volumetric determination of Phosphoric Acid by Acetate of Uranium* (Pincus, Journ. für Prakt. Chemie, lxxvi.)—A solution of phosphate of soda, the amount of phosphoric acid in which is accurately known, must be prepared; its strength should be such that each cubic centimètre exactly represents 0·01 of phosphoric acid. The acetate of uranium is prepared by dissolving pure ammonio-carbonate of uranium in acetic acid; it must be perfectly free from protoxide, to ensure which, the solution must be protected from the light. The strength of the solution is determined by pouring 5 to 10 cubic centimètres of the solution of phosphate of soda into a

beaker, adding ammonia, and an excess of acetic acid, and then pouring the solution of uranium from a burette with divisions of $\frac{1}{10}$th to $\frac{1}{20}$th cub. centim., stirring the mixture frequently during the process. The peculiar slimy precipitate of phosphate of uranium and ammonia is produced. From time to time a drop of the mixture is put upon a white porcelain plate, close to a drop of solution of ferrocyanide of potassium, and the two drops are allowed to flow together; as long as the phosphoric acid is not all precipitated, only a bluish-green colour is produced: but when the smallest excess of oxide of uranium is present, the spot which is at first bluish-green, becomes distinctly surrounded with a darker or lighter chocolate-coloured border: if the solution be very dilute, the reaction disappears again in a few minutes, after strong stirring; a further quantity of the solution of uranium must then be added. If the brownish-red colour has remained permanent for ten minutes, it does not again disappear, but makes its appearance still more distinctly, without any admixture of yellow and green, when, after the settlement of the slimy precipitate, a drop of the clear supernatant fluid is employed for the reaction. When it has been clearly ascertained by repeated experiments, how many cubic centimètres of the solution of uranium are necessary for the precipitation of 0·05 or 0·10 gramme of phosphoric acid, the solution may by calculation, and by adding water, be brought nearly to such a state of dilution that each cubic centimètre thereof may precipitate the phosphoric acid contained in one cubic centimètre of that solution, namely, 0·10 gramme. By repeated experiments, and by the addition of small quantities of water, or of a concentrated solution of oxide of uranium, it may be easily managed that the two solutions may be equivalent within the limits of $\frac{1}{10}$th to $\frac{1}{20}$th cubic centimètre, for quantities of 10 to 20 cubic centimètres; so that the highest possible error may lie within the limits of 0·0005 and 0·001 gramme of phosphoric acid.

To apply this method, the solution containing the phosphoric acid to be determined is mixed, whether neutral or acid, with ammonia, acetate of soda, and then with acetic acid in excess. Every $\frac{1}{10}$th cubic centimètre of solution of oxide of uranium employed until the production of the reaction, represents 0·001 gramme of phosphoric acid; the deposition of the precipitate is facilitated by heating the solution. The solution must not contain either protoxide of iron or alumina.

(5.) *Estimation as Phosphate of Bismuth* (Chancel, 'Comptes Rendus,' t. i.)—One part of pure crystalline subnitrate of bismuth ($BiO_3,NO_5+aq.$) is dissolved in 4 parts of nitric acid, sp. gr. 1·36, adding to the solution 30 parts of distilled water, and then boiling and filtering, if necessary. Each cubic centimètre of such solution will precipitate from 7 to 8 milligrammes of phosphoric acid. The substance to be analysed is dissolved in nitric acid, avoiding too great an excess; it is then diluted with distilled water, and the acid nitrate of bismuth added, until nothing more is precipitated. It is then boiled, filtered, and washed with boiling water, until the washings are no longer coloured by sulphuretted hydrogen. The precipitate is now carefully dried, and removed from the filter as completely as possible; the filter is incinerated by itself, and the residue added to the dried precipitate, which is then calcined.

The composition of phosphate of bismuth is:—

One equivalent of BiO_3	234·0	76·72
One ditto of PO_5	71·0	23·28
	305·0	100·00

Consequently the weight of the precipitate multiplied by 0·2328 will give the weight of the phosphoric acid in the substance analysed. If either chlorine or sulphuric acid be present, they must be removed before the nitrate of bismuth is added.

(6.) *Estimation of Phosphoric Acid, founded on the insolubility of Phosphate of Tin in Nitric Acid in the presence of Stannic Acid, and on the solubility of that compound in Sulphide of Ammonium.* (Girard, 'Bulletin de la Société Chimique de Paris.)

The substance is dissolved in nitric acid; when there are any difficulties in getting it into solution with this acid, it may be dissolved, first in any convenient reagent, and precipitated by ammonia; the well-washed precipitate then dissolves readily in nitric acid. Into the solution is thrown an indefinite quantity of *pure tin,* about four or five times the supposed weight of the phosphoric acid present, may be employed. The tin passes into the state of stannic acid, carrying down with it the whole of the phosphoric acid, as well as a great portion of the iron, and a little alumina; it is washed, first by decantation, and then on a filter; the filtrate and washings contain all the bases minus a portion of iron and alumina.

The precipitate containing the phosphoric acid, is redissolved

in a small quantity of aqua-regia, the solution supersaturated with ammonia, and then with excess of sulphide of ammonium.

The stannic acid and phosphate of tin immediately dissolve, leaving a black precipitate of sulphide of iron, containing alumina. It is allowed to stand for an hour or two, and then filtered, taking care to wash the precipitate with sulphide of ammonium, to remove the last traces of tin. It is then only necessary to add sulphate of magnesia to the filtered liquid, to obtain the characteristic precipitate of ammonio-phosphate of magnesia.

(7.) *Volumetric estimation of Phosphoric Acid by Perchloride of Iron* (Liebig's method modified by E. W. Davy. L. and E. Phil. Mag. and 'Chemical News,' vol. i. p. 181).—A standard solution of perchloride of iron is made by dissolving clean pianoforte wire in pure hydrochloric acid, and adding sufficient nitric acid to convert the protochloride into perchloride. Any free hydrochloric acid is then carefully neutralized with caustic ammonia, which is added until a little peroxide remains undissolved on shaking the mixture. Acetic acid is now added to dissolve the precipitated oxide, and when the solution is effected, it is largely diluted with distilled water, and graduated in the ordinary way, so that the amount of iron in a given quantity may be known. This solution may be kept a considerable time without undergoing any change. The phosphate to be analysed is dissolved in an acid, ammonia is added until the solution is decidedly alkaline, but not in large excess, and then a sufficient quantity of acetic acid to dissolve completely the precipitated phosphate, and leave a slight excess. The standard solution of iron is then added carefully from the burette, till the iron begins to be in slight excess, which is ascertained by taking a drop of the mixture (after it has remained a few minutes with occasional stirring) on a glass rod and touching with it a piece of thick filtering-paper placed over another piece which has been soaked in a solution of gallic acid and dried. The insoluble phosphate of iron is retained on the filtering-paper, and the solution which passes down to the lower paper, shows at once by the purple stain when sufficient iron has been added, and a minute excess exists in the mixture. If this excess be very minute, the stain will become more visible when the gallic paper is dried.* The results should be controlled by

* Instead of employing gallic acid to indicate the precise moment when the iron solution is in excess, a few drops of solution of *sulphocyanide of po-*

repeating this experiment a second and a third time, the phosphate being dissolved in a given quantity of solution, and a certain amount of it being taken for each determination.

The compound of iron and phosphoric acid has the invariable composition (Fe_2O_3, PO_5). In all cases, bibasic salts must be converted into tribasic, by heating with hydrochloric acid, and the solution must be allowed to cool before the estimation is made.

This method may be usefully applied to the determination of phosphoric acid in urine, in superphosphate of lime, and in manures generally.

(8.) *Estimation of Phosphoric Acid in Soils* (Schulze, 'Annalen der Chemie und Pharmacie,' vol. cix.).—About 50 grammes of the earth are ignited to destroy the organic matters, and then digested for a long time with hydrochloric acid. The filtered liquid is nearly neutralized with dilute ammonia, care being taken to avoid a permanent precipitation. To the solution, which should amount to about a pint and a half, 35 or 45 drops of terchloride of antimony are added, and it is set aside for 24 hours. During this time, there is deposited a yellowish-white flocculent precipitate which contains all the phosphoric acid, but is principally composed of antimonic acid carrying with it some oxide of iron and alumina; it contains, besides, a quantity of ammonia in proportion to that of the phosphoric acid.

The precipitate, well washed with distilled water, is boiled with soda ley containing a certain amount of silicate. After boiling, the liquor is filtered; the oxide of antimony changed into antimoniate of soda remains on the filter with the alumina and oxide of iron. The filtered alkaline solution which contains the phosphoric acid with a little alumina and silica, is supersaturated with hydrochloric acid and ammonia, concentrated by evaporation, again treated by ammonia, and filtered. The precipitate of alumina and silica thus obtained, carries with it a small quantity of phosphoric acid, to remove which, it is redissolved in a drop or two of hydrochloric acid, the solution evaporated to dryness, and the residue warmed with a little acidulated water. After having filtered again to separate the silica, a small quantity of tartaric acid is added to the filtered

tassium may be added to the solution of the phosphate before commencing the experiment. The solution will remain colourless until the whole of the phosphate is precipitated. But the blood-red colour characteristic of sulphocyanide of iron will make its appearance on the addition of a drop of the iron solution in excess.

liquor, which is then mixed with the preceding ammoniacal solution, containing the greater part of the phosphoric acid. From these solutions the phosphoric acid is separated as ammonio-magnesian phosphate in the usual manner.

(9.) *Estimation of Phosphoric Acid by Molybdate of Ammonia.*—According to Lipowitz (Pogg. Annal. der Physik und Chem. vol. clix.), to obtain accurate results by this method, the molybdate should be prepared by dissolving at a gentle heat, 2 parts of pure molybdic acid and 1 part of tartaric acid in 15 parts of water, and afterwards adding 10 parts of ammonia, sp. gr. 0·97, and 15 parts of nitric acid. The whole is heated to ebullition in a porcelain basin, whereupon about $\frac{1}{12}$th of the molybdic acid is deposited, which is separated by filtration.

In employing the above solution, the quantity of it thought necessary is placed in a capsule and heated to boiling, and then the liquid containing the phosphoric acid is added. The precipitate is washed with water acidulated with $\frac{1}{50}$th of nitric acid, and the filter is dried at 80° or 90° F. between folds of blotting-paper, or better still, over sulphuric acid. The composition of phospho-molybdate of ammonia is—

Molybdic Acid	90·744
Phosphoric Acid	3·142
Ammonia	3·570
Water	2·544
	100·000

(10.) *Separation of Phosphoric Acid from Bases by means of Nitric Acid and metallic Mercury* (H. Rose).—The phosphatic compound is dissolved in a sufficient quantity of nitric acid, the solution is conveyed to a porcelain dish, and so much metallic mercury added that a small portion is left undissolved by the free acid. It is then evaporated to dryness on the water-bath the dry mass again moistened with water, and again evaporated, this operation being repeated until the dry mass no longer smells of nitric acid while warm. It is next mixed well with water, filtered through a small filter, and washed till a few drops of the wash-water leave a residue, which disappears entirely on ignition. The filtrate contains all the bases combined with nitric acid together with nitrate of mercury, which is separated by hydrochloric acid; the solution is again filtered, and quickly washed, some chloride of ammonium having been previously added. If no iron or alumina are present, the alkalies,

lime, magnesia, and other metallic oxides existing as nitrates in the filtered liquid, are separated from each other in the usual manner; or the nitrate of mercury may be removed from the solution of the nitrates, by evaporating the solution in a porcelain dish, and exposing the residue to a red-heat in a platinum crucible. It should however be observed, that when alkaline nitrates are present, the dry residue on ignition must be mixed with a small quantity of dry carbonate of ammonia, in order to convert into carbonates, the free alkalies produced by the decomposition of the nitrates. If this precaution be neglected, the platinum crucible is very much acted upon. The calcined residue is dissolved in dilute hydrochloric acid, and the bases separated in the usual manner.

The phosphoric acid remains on the filter in combination with the mercury. There are likewise present nitrate and metallic mercury. The whole is well dried, removed from the filter, and mixed in a platinum crucible with an excess of carbonate of soda, the filter is rolled up and thrust into the mixture, which is then covered with a layer of carbonate of soda, and exposed for half an hour under a chimney to a moderate but not red heat, that the contents may not fuse. At this temperature the whole of the metallic mercury and the mercurial salts, with the exception of the phosphate, are expelled. The mass is now fused, and the fused mass treated with hot water, in which it dissolves entirely, if the operation has been conducted with care, and no iron were present. It is supersaturated with hydrochloric acid, and the phosphoric acid estimated as ammonio-magnesian phosphate. When *peroxide of iron* is present, the greater portion is left on treating the dry residue with water, with the phosphate of mercury, and only a small portion dissolves with the nitrates; it is filtered and washed in the usual way, the peroxide of iron in the solution determined with the other bases, and the insoluble portion fused with carbonate of soda. On treating the fused mass with water, the peroxide of iron is obtained perfectly free from phosphoric acid, whilst the entire amount of phosphoric acid in combination with soda is dissolved. When *alumina* is present this method becomes inapplicable.

Separation of Phosphoric Acid from Phosphorous and Hypophosphorous Acids (Rose).—The solution is poured gradually and in small quantities into a solution of chloride of mercury which must be fully saturated; a precipitate of subchloride of

mercury, exhibiting the splendour of mother-of-pearl, is determined, but its complete separation requires gentle digestion for several days: the subchloride of mercury is collected on a filter, dried by exposure to a gentle heat, and weighed.

From its weight it is easy to calculate how much oxygen has been taken up by the phosphorous or hypophosphorous acid to effect its conversion into phosphoric acid: hence the quantity of either of these acids is readily inferred. This quantity of oxygen is equivalent to the quantity of chlorine contained in the subchloride of mercury, since the chloride of that metal, on being converted into subchloride, loses exactly one-half of its chlorine. Another quantity of the solution to be analysed is treated with nitric acid, and a weighed quantity of oxide of lead, in the manner already described, the object being to determine the whole quantity of phosphoric acid, both that originally contained in the solution, and that formed from the phosphorous or hypophosphorous acid, at the expense of the oxygen of the nitric acid. Now, it is learnt by the first operation how much phosphoric acid is produced by the phosphorous or hypophosphorous acid of the solution, and, by deducting this from the whole quantity obtained by the second operation, the actual proportion of phosphoric acid in the solution analysed is known.

According to Wöhler, phosphorous acid is converted into phosphoric acid by being heated with sulphurous acid, sulphuretted hydrogen being formed and sulphur separated. In this manner he states that phosphorous acid may easily be detected in phosphoric acid: when arsenious acid is present at the same time, the sulphide of arsenic is immediately formed on treatment with sulphurous acid. Phosphorous acid in phosphoric acid may also be detected by Marsh's apparatus, by the phosphuretted hydrogen gas which is disengaged. The gas burns with a whitish flame, and when held close to a surface of porcelain, a green ring of light is observed in the expanded flame similar to that afforded by phosphorus when burnt in chlorine gas, or with an insufficient access of atmospheric air.

Analysis of Bone Earth.—Dissolve in hydrochloric acid, filter (if necessary), add oxalate of ammonia, and boil; then add excess of acetate of ammonia, and filter to separate the oxalate of lime; add tartaric acid to the filtrate, then ammoniacal sulphate of magnesia, and determine the phosphoric acid as pyrophosphate of magnesia.

194. Boron.

Quantitative determination of Boracic Acid (Stromeyer, Liebig Annalen, C. p. 80).—The boracic acid, if free, is combined with a sufficient quantity of potassa, pure hydrofluoric acid is then added in excess, and the whole is evaporated to dryness. Gelatinous *borofluoride* of *potassium* is produced, which subsequently forms hard, transparent crystals. The dry saline mass is then stirred up at the ordinary temperature with a solution of acetate of potassa of 20 per cent., and left to stand for some hours, when the fluid is passed through a weighed filter, and washed with the solution as long as the filtrate gives a precipitate with chloride of calcium. The acetate of potassa is then washed away with alcohol of specific gravity 0·851, and the salt is dried at 212° F. The presence of salts of the alkalies does not interfere with the method, but other bases must be separated, which is easily done in all cases by fusing the borates with carbonate of potassa. The borofluoride of potassium should be filtered through funnels made of gutta-percha or india-rubber, because the fluoride of calcium running away, attacks glass. The evaporation of the borate of potassa with hydrofluoric acid is effected in vessels of silver or platinum.

The composition of borofluoride of potassium is—

One equivalent of K	39·0 . .	30·95
One ditto of B	11·0 . .	8·73
Four ditto of F	76·0 . .	60·32
One ditto of (KF, BF_3) .	126·0 . .	100·00

Boracic acid may also be determined by adding to the solution a known quantity of pure oxide of lead, evaporating to dryness, igniting and weighing the residue: the amount of boracic acid is calculated from the increase of weight. Boracic acid, even when existing alone in a solution, cannot be estimated by evaporating to dryness, because although it is one of the most fixed of all substances at an intense heat, it possesses the property of volatilizing with the vapour of water or alcohol.

Separation of Boracic Acid from those fixed Bases with which it forms compounds decomposable by Sulphuric Acid.— The following method was proposed by Arfwedson:—A known weight of the compound is reduced to a fine powder, and

mixed in a platinum crucible with four parts of pure pulverized fluor spar. It is then moistened with sulphuric acid, and heated, first gently, and then gradually to redness, at which temperature it is maintained as long as fumes continue to be evolved. The whole of the boracic acid is thus driven off in the form of fluoride of boron ($BO_3+3FlH=BFl_3+3HO$). The bases, together with gypsum, remain behind, in combination with sulphuric acid; they are separated from each other according to the directions which have been given in the preceding pages, and the amount of boracic acid is calculated from the loss sustained by the original substance, after deducting from it the quantities of the different bases found; these determinations must therefore be made with great care, since the whole loss falls on the boracic acid.

When the bases with which boracic acid is combined are precipitable by sulphuretted hydrogen, or by sulphide of ammonium, these reagents are employed to separate them; their quantities must be accurately determined, and deducted from the weight of the compound submitted to analysis; the difference of weight is the quantity of boracic acid.

From the alkaline earths boracic acid is separated in the same manner as phosphoric acid, the amount of acid being calculated from the loss.

Determination of Boracic Acid in Silicates undecomposable by Acids (*Axinite, Tourmalines*).—The following process adopted by Gmelin, and given by Rose, is probably the best. The mineral is finely levigated, and heated strongly with carbonate of baryta. The ignited mass is treated with a sufficient quantity of hydrochloric acid to decompose it, and evaporated to dryness on the water-bath. The silica is separated from the residual mass in the usual manner, and the baryta precipitated from the filtered solution by carbonate of ammonia. The clear liquid is again evaporated to dryness and gently ignited; it is then weighed, and treated with alcohol and hydrochloric acid. The alcohol is inflamed, and in this way the boracic acid is got rid of; the residue is once more ignited and weighed, and the quantity of boracic acid is indicated by the loss of weight. Another method, recommended by the same chemist, is to ignite the pulverized mineral with carbonate of soda, and to treat the ignited mass with water. The solution having been digested with carbonate of ammonia, to remove the small portions of silica and alumina which the

water had dissolved, is evaporated to dryness; the dry mass treated with sulphuric acid, and then the boracic acid dissolved out by alcohol. The solution is finally saturated with ammonia, and the residue, which consists of boracic acid, is ignited and weighed.

Separation of Boracic Acid from Phosphoric Acid.—The phosphoric acid may be precipitated by sulphate of magnesia, and determined as pyrophosphate, or by Von Kobel's method, by the addition, first, of perchloride of iron, and then of carbonate of lime; not a particle of boracic acid is precipitated, but the separation of the phosphoric acid is complete.

195. Silicon.

Silicic Acid.—This acid is always converted from its soluble to its insoluble condition, for the purpose of weighing. The conversion is effected by evaporating the solution to dryness with hydrochloric acid, or any other volatile acid. The silicic acid is generally first obtained in a gelatinous state; but, by continuing the heat, it loses the whole of its water, and is brought to the condition of a dry powder. The evaporating mass must be constantly stirred with a glass rod during its exsiccation, to prevent spirting. The bases with which the silicic acid was combined, are separated by dilute acid, and the silicic acid, having been thoroughly washed and dried, is ignited in a platinum crucible, and weighed, when cold, with the cover on, the dry powder absorbing moisture rapidly from the air. The composition of silicic acid is—

One equivalent of Si	14·0	46·67
Two ditto of O	16·0	53·33
One ditto of SiO_2	30·0	100·00

Separation of Silicic Acid from Bases:—

Quantitative Analysis of Natural Silicates.—The great natural family of silicates may be arranged in three classes:—1st, those easily decomposable by hydrochloric acid; 2nd, those only decomposable by prolonged digestion with concentrated acid; and 3rd, those which absolutely resist the action of acids, even after prolonged digestion.

The following list of the names and composition of a series of interesting minerals belonging to each of these classes is taken from Rose's 'Treatise on Analysis' (English edition, translated by A. Normandy):—

1. *Silicates decomposable by Hydrochloric Acid in the Cold.*

		Combination of—
1.	Apophyllite . . .	Potassa, silica, lime, and water.
2.	Natrolite . . .	Silica, soda, and water.
3.	Scolezite . . .	Silica, alumina, lime, soda, and water.
4.	Mesolite . . .	Ditto ditto ditto.
5.	Mesole . . .	Ditto ditto ditto.
6.	Analcime . . .	Silica, alumina, soda, and water.
7.	Laumonite . . .	Silica, alumina, lime, and water.
8.	Potassa harmotone	Silica, alumina, baryta, potassa, and water; sometimes lime.
9.	Leucite . . .	Potassa, silica, and alumina.
10.	Eleolite . . .	Silica, alumina, lime, potassa, soda, and water.
11.	Brewsterite . . .	Silica, alumina, strontia, baryta, lime, and water.
12.	Sodalite . . .	Soda, silica, and alumina, with a small quantity of hydrochloric acid.
13.	Cronstedtite . . .	Silica, oxide of iron, and water.
14.	Ilvaite . . .	Silica, protoxide of iron, and lime.
15.	Gehlenite . . .	Silica, alumina, lime, and oxide of iron.
16.	Wernerite . . .	Silica, alumina, lime, and soda.
17.	Tabular spar . . .	Silica and lime.
18.	Nepheline . . .	Soda, silica, and alumina.
19.	Cancrinite . . .	Soda, silica, and lime.
20.	Mellinite . . .	Silica, magnesia, lime, and oxide of iron.
21.	Chabasite . . .	Silica, alumina, lime, and water, with a little potassa.
22.	Pectolite . . .	Silica, lime, soda, potassa, oxide of iron, and water.
23.	Okenite . . .	Silica, lime, soda, potassa, oxide of iron, oxide of manganese, and water.
24.	Davyne . . .	Silica, alumina, lime, iron, and water.
25.	Sodolenite . . .	Yttria, silica, glucina, oxides of cerium, and iron.
26.	Allophane . . .	Alumina, silica, and water.
27.	Helvine . . .	Silica, glucina, alumina, protoxide of iron and of manganese.
28.	Datholite . . .	Silica, boracic acid, lime, and water.
29.	Botryolite . . .	Differs from the preceding in containing one atom more water.

		Combination of—
30.	Haüyne	Potassa or soda, silica, alumina, lime, and sulphuric acid.
31.	Nosian	Sesquisilicate of alumina and soda (Klaproth).
32.	Lazulite	Silica, alumina, lime, oxide of iron, magnesia, soda, and sulphuric acid.
33.	Eudialite . . .	Silica, soda, zirconia, lime, oxides of iron and manganese, hydrochloric acid, and water.
34.	Orthite	Silica, alumina, oxides of iron, cerium, lanthanum, and manganese; lime, yttria, magnesia, and a small quantity of water.
35.	Electric Calamine	Oxide of zinc, silica, and water.
36.	Sideroschisolite .	Protoxide of iron, silica, alumina, and water.
37.	Hisingerite . .	Silicate of protoxide and sesquioxide of iron + six atoms of water.
38.	Dioptase . . .	Silicate of copper and water.
39.	Meerschaum . .	Magnesia, carbonic acid, silica, water, a little alumina, and traces of manganese and lime.
40.	Copper, Malachite	Carbonate and silicate of copper and water.

The above minerals, when finely pulverized, form a jelly when hydrochloric acid is poured upon them. The next nine do not form a jelly, and some of them are only decomposed by protracted digestion with hot hydrochloric acid. Nearly all these minerals resist altogether the action of acids after being ignited.

1.	Stilbite	Silicate of alumina, lime, and water.
2.	Epistilbite . . .	Ditto ditto.
3.	Heulandite . . .	Tersilicate of alumina and lime.
4.	Anorthite . . .	Silica, alumina, lime, and magnesia.
5.	Sphene or Pitanite	Tersilicate of lime and titanate of lime.
6.	Pyrosmalite . . .	Lime, tersilicate of oxide of iron and of manganese.
7.	Cerite	Hydrated silicate of peroxide of cerium.

	Combination of—
8. Cerine or Allanite .	Silicate of alumina and of cerium, of iron and of lime.
9. Pitchblende . . .	Uranium ore, containing from two to five per cent. of silica, probably in a state of mechanical, not chemical, combination.

Silicates only decomposable by Fusion with Carbonate of Potassa or Soda.

1. Felspar.	12. Mica.	26. Dichroite.
2. Albite.	13. Lepidolite.	27. Emerald.
3. Rhiacolite.	14. Talc.	28. Euclase.
4. Petalite.	15. Chlorite.	29. Phenakite.
5. Spodumene (Soda Spodumene).	16. Pinite.	30. Tourmaline.
	17. Achmite.	31. Axinite.
	18. Amphibole.	32. Topaz.
6. Oligoclase.	19. Anthrophyllite.	33. Chondrodite.
7. Labradorite.	20. Pyroxene.	34. Picrosmine.
8. Barytic harmotone.	21. Diallage.	35. Carpholite.
	22. Chatoyant or Schiller Spar.	36. Steatite.
9. Olivine.		37. Serpentine.
10. Prehnite.	23. Epidote.	38. Pumice stone.
11. Carbonated Manganese.	24. Idocrase.	39. Obsidian.
	25. Garnet.	40. Pitch stone.

To this class belong also the different species of false gems and artificial glass.

Silicates which resist the action of Acids and fusion with Alkaline Carbonates, but which are decomposed by ignition with pure Potash.

1. Zircon.	3. Cymophane.	5. Andalusite.
2. Cyanite.	4. Staurolite.	

Decomposition of Silicates by Acids.—The mineral is reduced to the finest possible powder in an agate mortar. It is dried at 212°, avoiding a higher temperature, because many of these compounds contain water and other volatile matters which must not be expelled; and because, moreover, an elevated temperature might interfere with the readiness with which the silicate is decomposed by acids. The pulverized mineral, having been deprived of its hygrometric water, is weighed in a platinum or porcelain dish, and digested at a gentle heat until complete de-

composition has taken place, which is known by rubbing a glass rod against the bottom and sides of the vessel; if it produce a grating noise it shows that the decomposition is not complete, and the digestion must be continued till the end of the rod glides smoothly over the bottom of the dish. The separated silicic acid does not, in all cases, assume the same appearance, as was remarked above; sometimes it separates in a bulky gelatinous state, in other cases no jelly is formed, the acid being liberated in the form of a fine powder: some silicates, again, are decomposed almost instantaneously, while others require long-continued digestion. The operator must bear all these facts in mind; and, above all, he must assure himself of the complete decomposition of the mineral, or all his time and labour will have been expended in vain. The decomposition being complete, the mass is evaporated to dryness on the water-bath, and the residue heated until all moisture is expelled; the dry mass is then digested with hydrochloric acid, which dissolves out all the bases, leaving the silicic acid in its insoluble modification: it is collected on a filter, washed with boiling distilled water, dried, ignited, and weighed. The filtrate and the washings are quantitatively examined for bases, according to the instructions given in the last chapter. Rose objects to the evaporation of the silicate to dryness after its decomposition by hydrochloric acid, partly on the grounds that the whole of the silica is not thereby rendered insoluble, and that portions have still to be separated in the course of the analysis, but chiefly because it is possible that during the evaporation, certain volatile constituents of the compound may be expelled, and thus escape detection, which, he says, has happened with many chemists who have pursued this method. Compounds which are easily decomposed by hydrochloric acid, should never, according to this eminent chemist, be exposed to heat, but digested with cold acid, only employing heat when the decomposition will not proceed without it. In cases where the silicic acid is separated in the gelatinous form, Rose treats the mass with water, and thus separates the silicic acid in light flocks. Most chemists, however, prefer the method of evaporating the whole mass at once to dryness; it is the simplest, and on the whole the least troublesome, and if the mass has been thoroughly exsiccated, there is very little fear of any of the silicic acid finding its way again into the solution. In the case of those minerals which contain volatile constituents, their nature will generally be

made known by the preliminary examination, and the course of analysis will be shaped accordingly; it is evident, however, that these particular cases cannot come within the limits of a description of a general method, to which the above instructions must be understood to apply.

(2.) *Decomposition of Silicates by fusion with Alkaline Carbonate.*—The mineral reduced to the finest possible state of division, (by elutriation if necessary,) is mixed in a platinum crucible with from three to four times its weight of pure anhydrous carbonate of soda, or with an equal quantity of well-dried and previously pulverized carbonate of potassa, or, which perhaps is still better, with a mixture of the two carbonates in the proportion of single equivalents, such as is obtained by calcining Rochelle salt (tartrate of potassa and soda), lixiviating the calcined mass in water, and evaporating the solution to dryness. The mixing of the pulverized mineral with the alkaline carbonate is made by a rounded glass rod; it must be very intimate, and all portions adhering to the rod must be carefully wiped off into the crucible. The cover is placed loosely on the crucible, and it is gradually raised to intense ignition, at which it must be maintained from thirty minutes to an hour; at the end of this time the mass will be either completely fused, or in a state of semi-fusion, according as the mineral contains more or less silicic acid. The contents of the crucible when cold, are transferred to a beaker, which can be covered with a glass plate. When the mass has only been in a state of semi-fusion, it is generally easily removed by bending and pressing the sides of the crucible; but when the fusion has been complete, it is sometimes not very easy to remove it without having recourse to hydrochloric acid: in the event of this being necessary, the crucible should be placed in a large beaker before the acid is poured on it, in order to avoid loss by the sudden evolution of carbonic acid. The contents of the crucible being safely lodged in the beaker, the mass is drenched with water, and hydrochloric acid added cautiously, to prevent too violent an effervescence; it is then covered with its plate, and exposed to a gentle heat until perfect solution has taken place, or until only slight flakes of silica are seen floating in it, by which it is known that the decomposition of the mineral has been complete. If, on the other hand, a heavy gritty powder should subside to the bottom of the vessel, the operator hereby learns that, either from not having been in sufficiently fine a state of division, or from the heat not having

been sufficiently intense or long continued, or from some other cause, the mineral has not been entirely decomposed; and the powder must be carefully collected, washed, dried, and weighed, and the weight deducted from the quantity originally taken; or, which is always best, the whole experiment must be recommenced with a fresh portion of substance. Supposing, however, the decomposition to have been successfully performed, the silica is separated by evaporation to dryness on the water-bath, and the analysis proceeded with precisely in the same manner as in the case of a silicate, decomposable by simple digestion with hydrochloric acid.

It must be observed that the silicic acid, as separated from minerals of difficult decomposition, may contain a considerable quantity, 12 or 15 per cent. of *alumina*, and still form a transparent glass when fused with soda. It is always necessary, therefore, to examine the silica obtained from such minerals very carefully for that earth, with which view it is fused with carbonate of potassa, the melted mass treated with hydrochloric acid, and the solution evaporated to dryness. The dry mass is moistened with hydrochloric acid, and afterwards treated with water. The acid solution, filtered from the undissolved silicic acid, is now supersaturated with ammonia. If the solution give no precipitate, the silicic acid may be considered to have been pure; but, if a precipitate be formed, this can only arise from an impurity, which, in most cases, will prove to be alumina.

(3.) *Decomposition of Silicates by Hydrofluoric Acid.*—The finely powdered mineral is placed in a shallow platinum dish *b*, supported on a lead tripod, standing in the centre of a lead dish *a*, Fig. 77, about six inches in diameter. The bottom of this lead vessel is covered to the depth of from one-eighth to one-fourth of an inch, with a mixture, made to the consistence of paste, of powdered fluor-spar and sulphuric acid. The dish is provided with a flat cover, made of the same metal. The mineral to be decomposed is moistened with a little water, and the cover having been placed on the dish, the latter is gently heated over the sand-bath underneath a flue; hydrofluoric acid is liberated, by means

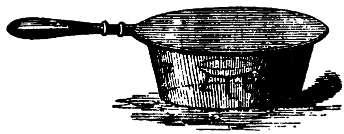


Fig. 77.

of which from 20 to 30 grains of siliceous mineral may be completely decomposed in the course of an hour and a half. During the process, the powder must be twice moistened with a few drops of water; if it be well spread out on the platinum dish, it is unnecessary to stir it. When the operation is finished, concentrated sulphuric acid is added, drop by drop, to the powder, as long as hydrofluosilicic acid is given off; a gentle heat is at the same time applied, and finally the excess of sulphuric acid is driven off by continued heat and evaporation to dryness. The dry residue, after being moistened with hydrochloric acid, is boiled in water, and further examined in the usual way. This method is particularly applicable to the examination of such minerals as contain alkalies: or the finely pulverized silicate may be digested with rather concentrated hydrofluoric acid and a gentle heat, sulphuric acid added cautiously in excess, and the mixture evaporated to dryness, first on the water-bath and afterwards at a higher temperature, until the excess of sulphuric acid is expelled. If, on the addition of water aided by heat, the dry residue be completely dissolved, the decomposition of the silicate is complete; if, on the contrary, a residue remain, this must be again treated with hydrofluoric acid. The evaporation must be conducted under a hood so as to carry off the fumes of hydrofluoric acid, which are very corrosive and injurious.

Another method of analysing such silicates, proposed by Abich, is to fuse them with hydrate of baryta or with carbonate of baryta, using from 4 to 6 parts of the carbonate to 1 of the mineral; the most intense heat is required, no action taking place till a state of fusion has been induced; but, when once the action has commenced, it goes on rapidly and energetically, and the operation is finished in a quarter of an hour. No silicate has yet been found to withstand the action of this agent, but the most powerful heat attainable in a wind furnace of the best construction is required. When hydrate of baryta is employed, the operation may be conducted in a silver crucible over a good spirit lamp; from 4 to 5 parts of the hydrate, deprived of its water of crystallization, are mixed intimately with 1 of the powdered mineral, and the mixture is then covered with a layer of carbonate of baryta. The decomposition being complete, the analysis is proceeded with in the usual manner.

Fluoride of ammonium may also be employed for the decomposition of silicates; it is made by saturating hydrofluoric acid

with ammonia. The impure acid which generally contains some fluoride of silicon, lead, and iron, will answer for the purpose. A small quantity of carbonate of ammonia and sulphide of ammonium must be added to the solution, which after a time is decanted and evaporated in a platinum crucible. During the evaporation, a small piece of carbonate of ammonia must be added from time to time; when the mass becomes pasty, it must be stirred with a spatula; when well dried, the salt may be kept in vessels of platinum, silver, or gutta-percha.

To apply this salt to the analysis of silicates, Rose directs thus (Poggendorff's Annalen der Physik und Chem., vol. cviii.). Mix the finely pulverized mineral with six times its weight of the fluoride in a platinum crucible; add a little water, and heat at first gently, and then to bright redness, and continue the heat as long as vapours are disengaged. Treat the residue with sulphuric acid, and drive off the excess of this acid by evaporation. When the sulphates formed are not completely dissolved by water acidulated with hydrochloric acid, the insoluble residue must be treated with a fresh portion of the fluoride. The temperature should not be raised too high during the operation, for in that case, if the silicate contain alumina, a fluoride of aluminum will be formed difficult to decompose by sulphuric acid.

(4.) *Decomposition of Silicates by fusion with Carbonate of Lime and Chloride of Ammonium* (Lawrence Smith, 'Silliman's Journal,' July, 1853).

Mix intimately in a glazed mortar, one part of the finely pulverized mineral with five or six parts of carbonate of lime, and half to three-fourths of pure chloride of ammonium; introduce the mixture into a platinum crucible, and heat to bright redness from thirty to forty minutes. There is no silicate which after having undergone this process is not easily dissolved by hydrochloric acid. For the action of the lime to have been complete, it is not necessary that the mass should have settled down to perfect fusion. The contents of the crucible are dissolved in dilute hydrochloric acid, and the solution evaporated to dryness, the operation may be completed over a lamp without the danger of the *spitting*, which occurs when the fusion is made with soda. To the dry mass hydrochloric acid is added, it is then diluted and boiled; when cold, carbonate of ammonia is slowly added in excess, and the precipitate which occurs is filtered off. The filtrate contains chloride of ammonium, chlorides of calcium, and perhaps of magnesium, and the alkalies

of the mineral. It is concentrated by evaporation, and nitric acid added in the proportion of about three parts to every one of chloride of ammonium, the latter is completely decomposed by the nitric acid at a low temperature, into gaseous products, and much trouble is avoided, the evaporation proceeding rapidly. When dry, the residue is dissolved in water, lime water is added, and the liquid is boiled and filtered. To the filtrate, a sufficient quantity of carbonate of ammonia is added to separate the lime, which is filtered off, and the filtrate is again evaporated to dryness. Dilute sulphuric acid is now added, by which the nitric and hydrochloric acids are expelled, and the alkalies remain in the form of sulphates. For the conversion of the alkaline sulphates into chlorides, acetate of lead is added in slight excess, in order to precipitate the sulphuric acid; the sulphate of lead is filtered off; the lead is removed from the filtrate by sulphuretted hydrogen, the sulphide of lead is filtered off, excess of hydrochloric acid is added to the filtrate, by which the acetates of the alkalies are converted into chlorides, and the liquid is evaporated to dryness. When the object is the quantitative estimation of the *alkalies* only, in the siliceous compound, (analysis of soils, cinders, etc.) the above operations may be considerably curtailed. After the mineral or product under examination is perfectly decomposed by fusion with carbonate of lime and chloride of ammonium, the mass is heated with water *alone*, until thoroughly disintegrated, when it is thrown upon a filter, and thoroughly washed. The filtrate contains merely the chlorides of the alkalies, a little chloride of calcium, and caustic lime. A small quantity of carbonate of ammonia is added to precipitate the two latter substances, the carbonate of lime is separated by filtration, the filtrate is evaporated and gently ignited, and the residue consists of the alkalies in the state of chlorides.

196. Carbonic Acid.

(1.) *Quantitative determination of Carbonic Acid in a free state in aqueous solution.*—This is very conveniently effected by adding to a weighed or measured quantity of the solution, a clear mixture of chloride of barium and excess of ammonia; the latter absorbs the carbonic acid, and carbonate of ammonia is formed which, reacting with the chloride of barium gives rise to chloride of ammonium and carbonate of baryta: the latter is precipitated. It is collected on a filter and washed with water, to which am-

monia has been added; the funnel must be carefully protected from the air during filtration, otherwise carbonic acid might be absorbed, which would increase the amount of carbonate of baryta.

The precipitate having been well washed, is dried and gently ignited, together with the filter, it may then be weighed, and the amount of carbonic acid calculated from the weight of the carbonate of baryta; but should the original solution contain any substances which might also be precipitated by ammonia, and chloride of barium, the amount of carbonic acid in the precipitate should be determined in the apparatus of Will and Fresenius (Fig. 69, p. 268). A process for determining the amount of free carbonic acid in a water, apart from that which is combined with lime and magnesia in the form of soluble bicarbonates, has been suggested by M. Gaultier de Claubry (Comptes Rendus, vol. xlviii.). It consists in passing through the water a current of atmospheric air which has been freed from carbonic acid; the free carbonic acid in the water only is removed, the bicarbonates remaining in solution; after passing through the water, the air is dried and then passed through a weighed Liebig's potassa-bulb.

(2.) *Estimation of Carbonic Acid in the gaseous state.*—The volume of gas is first accurately measured in a graduated tube standing over mercury; a small piece of moistened caustic potassa, attached to a piece of ignited iron wire, is then passed through the mercury into the tube; when the absorption has ceased, the potassa is withdrawn, and the volume of the unabsorbed gas accurately determined: the difference in the two measurements indicates the quantity of carbonic acid. When the volume of the gas is large, and contained in a receiver which is not graduated, it is sometimes determined by the increase in weight of a piece of caustic potassa passed into the receiver, and allowed to remain for some time in contact with the gas.

(3.) *Estimation of Carbonic Acid in Aerated Waters.*—A piece of india-rubber tubing *a* (Fig. 78) is attached to a cork borer 5 or 6 inches long, having small holes pierced in its sides; a bent tube leading into a flask containing pure ammonia, is securely connected with the other end of the vulcanized tube. On boring the cork the plug carried down stops the tube until the lateral holes come below the lower surface of the cork, when effervescence commences, the liberated car-

bonic acid being absorbed by ammonia. As soon as all visible action has ceased, the vessels are disconnected, and the contents of the bottle emptied into the flask containing the solution of ammonia; chloride of barium is then added, and the whole is boiled. The amount of carbonic acid in the precipitate is de-

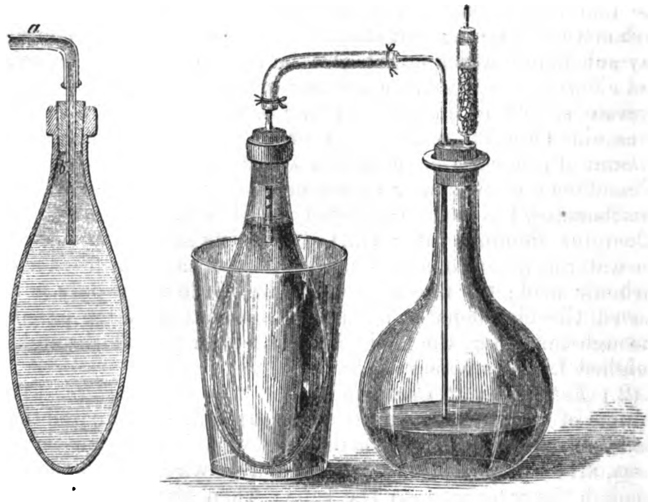


Fig. 78.

termined in the apparatus of Will and Fresenius. This represents the total quantity of carbonic acid, free and combined. To ascertain the quantity in the latter state, the contents of a similar bottle of the water are evaporated to dryness, the residue is very gently ignited, and the amount of carbonic acid determined; this is deducted from the total quantity found by the first experiment; the difference is the weight of the carbonic acid existing in the water in a gaseous state.

Analysis of Carbonates.—We have already described at some length the method which is easiest of execution, and which, on the whole, gives the most satisfactory results, viz. that of Fresenius and Will. Fig. 79 shows a little apparatus that may sometimes be conveniently employed. It consists of a small thin-bottomed flask, capable of containing about four

ounces of water. It is fitted with a cork, through which is inserted a bent tube adapted to another wide tube, containing fragments of dried chloride of calcium; the extremity of this tube is drawn out to a capillary orifice. The small tube seen inside the flask is intended to hold the sulphuric or hydrochloric acid, with which it is proposed to decompose the carbonate. It should rest against the side of the flask at an angle of about 45° from the bottom, so that by inclining the flask the whole of the acid can be made to flow out. The carbonate to be analysed is accurately weighed, and projected into the flask, which should contain about an ounce of water; and, the chloride of calcium tube having been fixed air-tight into its place, the whole apparatus is accurately weighed. Great care must be taken that none of the acid in the tube comes into contact with the carbonate before the operation is commenced. Everything being ready, the flask is inclined so as to allow a portion of the acid to flow out of the tube; effervescence immediately takes place, carbonic acid is expelled, and escapes through the orifice of the chloride of calcium tube, being thoroughly dried during its passage through the lime salt. As soon as the effervescence has ceased, a fresh portion of acid is caused to flow out of the tube, and the operation is repeated until no further escape of carbonic acid gas is perceived.

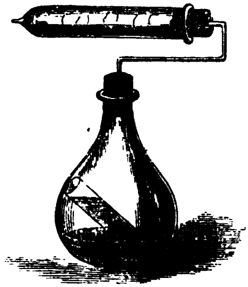


Fig. 79.

The flask is now placed in a vessel of boiling water, where it is allowed to remain for some time in order to expel all the carbonic acid in the liquor, and in the upper part of the flask, aqueous vapour is prevented from escaping by the chloride of calcium. On cooling, atmospheric air finds its way into the flask, which is thus brought to the same condition it was in, previous to commencing the experiment. It is now weighed; the loss of weight indicates the amount of carbonic acid. This is a very convenient little apparatus for the analysis of limestones and marls.

Many other forms have been given to this apparatus; that by F. Mohr, shown in Fig. 80, is neat, light, and convenient. The acid with which the carbonate is to be decomposed is con-

tained in the bulb, it is introduced into the flask, containing the carbonate to be decomposed, by relaxing the india-rubber tube adapted to the upper end, by the compression of the clamp; the exit tube is filled with fragments of chloride of calcium.

Fig. 80.

Another form of apparatus is shown in Fig. 81. The acid is contained in the test-tube, which is connected with the flask containing the carbonate to be analysed by the siphon *b*, *a*; by applying suction at *d* the acid is introduced into the flask, and the liberated carbonic acid gas escapes through the chloride of calcium tube *c*, by which it becomes dried.

Mohr's apparatus is represented in Fig. 82; it is especially adapted for determining the amount of carbonic acid in the carbonates of the metallic oxides, and in mortars, cements, etc. The weighed substance is introduced into the flask *b*, together with some water, and a little tincture of litmus; *d* contains strong hydrochloric acid. The flask *a* is about one-eighth filled with solution of ammonia, free from carbonic acid, and the tube *c* contains fragments of coarsely pounded glass, moistened with the same liquid. Everything being arranged, and the apparatus having been proved to be tight, the clip of the tube *d* is relaxed so as to allow the acid to flow

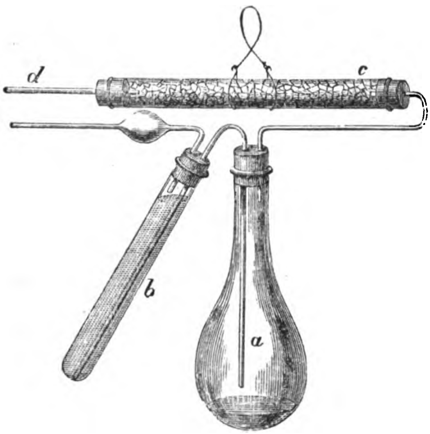


Fig. 81.

gradually into *b*, which should then be gradually heated till the liquid boils; it is allowed to cool, and again boiled, and the same operation is several times repeated, until it is certain that

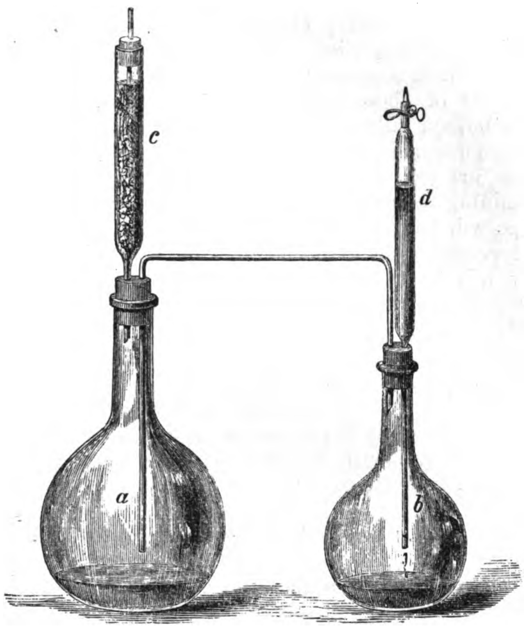


Fig. 82.

the whole of the carbonic acid has been carried into the flask *a*. The liquid in *b*, at the end of the operation, must be intensely red, and the end of the siphon-tube must not reach the surface of the ammonia solution in *a*. When the apparatus is cold, it is taken apart; solution of chloride of barium is added to the contents of *a*, which are then boiled, rapidly filtered, and the amount of carbonic acid in the precipitate determined in the usual manner.

The analysis of a great many solid carbonates may be effected by simply igniting them, and estimating the amount of carbonic acid from the loss of weight; it is, of course, indispensable that the substance shall contain no other volatile

constituents, which may be expelled by the ignition, together with the carbonic acid. It is also necessary that the substance from which the carbonic acid is expelled shall not itself undergo any alteration, whereby it may be either increased or diminished in weight. The carbonates of certain metallic oxides are in this condition; as, for example, the carbonates of protoxide of iron and of manganese, and of oxide of cobalt. The analysis of these salts may be performed by igniting them in a bulbed tube of hard glass, through which a stream of dry carbonic acid gas is passing. Carbonates which contain water, are analysed by the same process which is adopted in determining the carbon and hydrogen in organic substances, and which will be fully described hereafter.

The decomposition of carbonates by heat is greatly facilitated by mixing them with about four times their weight of finely powdered borax, as was first pointed out by Count F. Schaffgotsch (Poggendorff's 'Annalen'). He did not find anhydrous boracic acid so convenient for the purpose, since by long melting this acid decreases slowly but constantly in weight. The anhydrous biborate of soda, or glass of borax, is, however, absolutely fixed, and is well adapted for the purpose, from the ease with which it decomposes the carbonates in fusing, and from its causing no ebullition on account of its thick fluidity.

Separation of Carbonic Acid from Sulphurous Acid.—For this purpose Persoz introduces into a graduated tube containing the mixed gases, a glass rod covered with starch paste, and coated with powdered iodate of potassa or soda; the sulphurous acid is hereby converted into sulphuric acid, and as soon as no further decrease in the quantity of the confined gas is perceptible, the glass rod is removed, and the residual gas immediately measured. Before, however, the carbonic acid can be considered as free from sulphurous acid, another glass rod must be introduced, which is also covered with the paste made with starch and a dilute solution of iodate of potassa; if the least trace of sulphurous acid exist in the gas, the rod is instantly coloured blue. This method is therefore well adapted for the detection of minute traces of sulphurous acid.

Separation of Carbonic Acid from all other Acids.—As carbonic acid is readily removed from its combinations by heating with stronger acids, its separation from most other electro-negative bodies is attended with but little difficulty. The

carbonic acid is determined in one portion of the compound, and the other acids in another portion. If the substance under examination contain fluorides, the carbonic acid is expelled by one of the weak non-volatile acids, such as tartaric or citric acid; since, if sulphuric or hydrochloric acid were employed, hydrofluoric acid would, at the same time, be discharged. When there occurs in the course of an analysis, a mixed precipitate of fluoride of calcium and carbonate of lime, Fresenius directs the separation of the two substances to be effected by pouring acetic acid over the mixed precipitate, adding alcohol, filtering, and finally washing the residue with alcohol.

Separation of Carbon from Nitre and Sulphur: Analysis of Gunpowder.—The sample intended for analysis (from 20 to 30 grains) is finely pulverized and dried, either in the water bath, or *in vacuo* over sulphuric acid, in the manner shown in Fig. 59, p. 247. It is then digested for some time with boiling distilled water, and the insoluble portion thrown on a filter, the weight of which is known. It is repeatedly washed while on the filter with hot water. The filtrate and the washings are evaporated to dryness, and the dry mass estimated as nitre; or, after having weighed the residue, it may be redissolved in water, and tested for common salt by nitrate of silver, and, if any notable quantity is thereby indicated, the silver salt must be added as long as any precipitation takes place, and the resulting chloride of silver calculated into its equivalent of chloride of sodium, and the amount deducted from the dry salt. The substance remaining on the filter is dried and weighed; it consists of carbon and sulphur. To determine the proportion of these two elements, a fresh quantity, (from 15 to 20 grains,) of the finely powdered sample, is intimately mixed with an equal amount of pure anhydrous carbonate of soda; the mass is then mixed with about eight parts of nitre, and six of common salt. The whole is strongly heated in a platinum crucible: the sulphur becomes hereby oxidized into sulphuric acid at the expense of the oxygen of the nitric acid, and the acid thus formed unites with the potassa of the decomposed nitre, forming sulphate of potassa. As soon as the mass has become white, it is dissolved in water, acidified with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium; from the weight of sulphate of baryta obtained, the amount of sulphur is calculated.

Marchand modifies the above (Gay-Lussac's) method of estimating the sulphur in gunpowder in the following manner:—A

mixture of 1 part of nitrate and 3 parts of carbonate of baryta is intimately mixed with a twelfth part of the powder, and heated in a tube closed at one end. A layer from 3 to 4 inches in length of baryta salt is inserted in front of the mixture, and the whole is heated in the combustion furnace, beginning at the anterior portion. The mixture, which does not fuse, is easily removed from the tube, which is rinsed with dilute hydrochloric acid, in which the ignited mass is then dissolved. The liquid is retained in a beaker for several hours near 212°, and the sulphate of baryta is then collected on a filter. The amount of sulphur may likewise be determined accurately in the moist way. From 30 to 40 grains of the powder are treated in a flask with concentrated nitric acid, with the addition of a few grains of chlorate of potassa; the mass is kept gently boiling, until at last, a colourless liquid is obtained, which is diluted with a large quantity of water, and precipitated while hot with chloride of barium.

M. Cloëz and Guignet employ as an oxidizing agent, pure crystallized permanganate of potassa. About one gramme of the well-dried powder is boiled with a saturated solution of the permanganate, fresh portions being added from time to time, until the mixture has a persistent violet colour: concentrated hydrochloric acid is then added, and the whole boiled until the oxide of manganese is completely dissolved; the solution is filtered, concentrated (if necessary), a little nitric acid added, and the sulphuric acid precipitated by chloride of barium.

The charcoal is estimated *indirectly* by deducting the weights of the moisture, nitre, and sulphur, from the original weight of the powder analysed.

The amount of nitre in gunpowder may, according to Marchand, be ascertained with great precision, by determining the quantity of nitrogen in the powder. For this purpose a portion of the sample is weighed off, reduced to a fine powder, and intimately mixed with oxide of copper; the mixture is transferred to a combustion tube, the sealed end of which is charged with carbonate of lead, and then with oxide of copper; oxide of copper and metallic copper are placed in front. The details of the process will be given hereafter.

Uchatius employs the following ingenious process for determining the amount of nitre. 20 grammes of the powder are introduced into a flask with about 50 grains of lead shot; 200 grammes of well water are then added by means of a graduated pipette;

the flask is well closed and shaken for eight minutes, by which the solution of the nitrate of potash in the powder is completely effected. The solution is filtered, and 172 grammes of the filtrate measured off in a second pipette, and placed in a narrow beaker; it is brought to the normal temperature, and a glass bubble is introduced. This bubble is so constructed that when the powder contains 75 per cent. (= 15 grammes of nitrate of potassa) it will rise to the surface, while the addition of three or four drops of water will cause it to sink to the bottom. By means of a graduated pipette, fixed quantities of one of two solutions is added, so as to cause an increase or diminution in the quantity of nitrate of potash contained in the solution, equal to one or more tenths per cent. until the bubble attains the surface of the solution. The percentage quantity of nitre in the gunpowder is now ascertained by adding to, or deducting from, 75, the amount of diminution or increase in the strength of the solution effected by the addition of the test fluid.

Separation of the Sulphur from the Charcoal.—For this purpose Marchand adopts Wöhler's method, which is as follows:—A weighed quantity (about 20 grains of the dried mixture of sulphur and charcoal) is introduced into a bulb blown out about 2 inches from the extremity of a tube of hard glass, about 8 inches in length. An asbestos plug is thrust into the longer part of the tube to within half an inch or so of the bulb, and the remainder of the tube is then filled with metallic copper; the tube is then weighed, a current of dried carbonic acid gas is passed through the tube, and the part containing the copper having been raised to a full red-heat, the sulphur is distilled through it; the sulphur vapours combine with, and are retained by, the copper; when the operation is over, the tube is allowed to cool, it is cut off between the asbestos plug and the bulb, and the latter containing the carbon is rapidly weighed; the loss of weight expresses the amount of sulphur. The heat which must be applied to remove the whole of the sulphur from the charcoal is, in general, greater than that at which the charcoal had been prepared, and there is observed during the expulsion of the sulphur a strong odour of humic acid; carbonic acid, carbonic oxide, and water are also expelled. Instead of distilling the sulphur from the charcoal, it may be removed by solvents. Marchand employs for this purpose *sulphide of carbon*. After exhausting the gunpowder with water, which he effects in a displacement apparatus of the form of an ordinary chloride of

calcium tube, from 7 to 8 inches long, the bulb being stopped with asbestos, he treats it with absolute alcohol, which displaces the water, upon which sulphide of carbon, which has been rectified over oxide of lead, is poured over it until what passes through, leaves no sulphur on evaporation; the powder is then finally treated with alcohol. It is still better to use the sulphide of carbon mixed with absolute alcohol. As soon as the charcoal is washed, a current of dry air is drawn through the tube by means of an aspirator, the tube itself being confined in an air bath at 248°. The dry charcoal is weighed accurately in the tube.

The sand, etc., contained in the powder may be determined with tolerable accuracy by trituration and suspension.

197. Oxalic Acid.

The quantitative estimation of this acid may be effected by precipitating it from its solutions in the form of oxalate of lime, and determining the latter as carbonate or sulphate; or by ascertaining the amount of carbonic acid yielded by its decomposition.

Quantitative Estimation of Oxalic Acid by precipitation.—The acid, if in a free state, is neutralized as exactly as possible with ammonia, diluted with water, and chloride of calcium mixed with acetate of soda added; the precipitated oxalate is well washed, dried, and ignited, with the precautions prescribed page 279, by which it is converted into carbonate; and the quantity of oxalic acid is calculated from the weight of the latter, every equivalent of oxalic acid yielding two of carbonic acid, thus:—

$$C_2O_3 + O = 2CO_2.$$

There are two ways of estimating the amount of carbonic acid yielded by the decomposition of oxalic acid; one is by burning it with oxide of copper, according to the ordinary method of organic analysis; and the other, which is by far the most convenient and expeditious, is by neutralizing it with ammonia, and bringing it into contact with peroxide of manganese and sulphuric acid, in the manner fully described, under the head of Manganese, page 338. 9 parts of oxalic acid require theoretically 11 parts of manganese, but an excess of the latter does no harm. Both of these latter methods are applicable to the determination of oxalic acid in the oxalates. When the oxalate is soluble in water, the amount of oxalic acid may be

determined by precipitation, as carbonate of lime, and the base or bases with which it was combined, determined in the filtrate by appropriate methods. Many of the insoluble oxalates may be analysed by simple ignition, the bases being left either as pure metals, or as oxides, or as carbonates. Oxalates, the bases of which are precipitated by carbonate of potassa, may be decomposed by boiling for some time with that alkali; oxalic acid is thus brought into a soluble state, in the form of oxalate of potassa, and may be precipitated by a neutral solution of lime.

Oxalic acid, as met with in commerce, frequently contains *tartaric acid* and *sulphate of potassa.* The former is detected by digesting a portion of the acid in a test tube with concentrated sulphuric acid; it should remain colourless; but if tartaric acid be present, it turns black, that acid being decomposed. The presence of sulphate of potassa is indicated by a precipitate insoluble in nitric acid, produced on adding to a solution of the suspected acid a few drops of chloride of barium.

CHLORINE.

198. Hydrochloric Acid.

The quantitative determination of this acid is generally effected by precipitating its chlorine in the form of chloride of silver; for the composition of this salt, and for the precautions to be observed in its precipitation, the student is referred to section 174. If hydrochloric acid alone be present in aqueous solution, it may be estimated in the form of sal-ammoniac, by adding ammonia in excess, evaporating the solution to dryness, and performing the exsiccation of the residue on the water-bath.

Soluble chlorides are analysed by first precipitating the chlorine by nitrate of silver, and then, after removing the excess of the silver salt from the filtrate by hydrochloric acid, estimating the amount of base or bases by the ordinary processes.

The analysis of the compounds of chlorine with *tin* and *antimony*, is performed in a somewhat different manner. If a solution of nitrate of silver were added to a solution of perchloride of tin, there would be precipitated, besides chloride of silver, a compound of peroxide of tin with oxide of silver, which would vitiate the result. It is necessary, therefore, to remove the base from the solution before attempting to precipitate the electro-negative element; this is done by passing through the

solution, contained in a flask which can be corked, a stream of sulphuretted hydrogen, and, when it is saturated, allowing it to repose for a considerable time; the sulphide of tin is filtered off as soon as it has completely subsided, and the excess of sulphuretted hydrogen removed from the filtrate by mixing it with a solution of sulphate of copper;—this is indispensable; otherwise, on the addition of nitrate of silver, a precipitate both of chloride and of sulphide of silver would take place. The excess of sulphuretted hydrogen being removed, the solution is precipitated by nitrate of silver in the usual manner. In the case of chloride of antimony, it is unnecessary to remove the base previous to determining the chlorine; but the precaution must be taken of mixing the solution with a sufficient quantity of tartaric acid to prevent the formation and precipitation of a basic salt.

Such chlorides as are insoluble, or only sparingly soluble in water, but soluble in nitric acid, are dissolved in the latter, the solution diluted with water, and precipitated by nitrate of silver in the usual manner.

Analysis of Chlorides insoluble in Water and in Nitric Acid.—This may be performed in three ways:—1st, by reducing them to the metallic state by ignition in a stream of dry hydrogen gas: 2nd, by fusion with alkalies; and 3rd, by digestion with caustic potassa.

(1.) *By reduction.*—The apparatus, Fig. 71, p. 303, may be employed. The chloride to be analysed (chloride of lead for instance) is accurately weighed in the little bulb *d*, a stream of dry hydrogen gas from the bottle *a* is conducted over it, and the bulb is then heated to redness by means of a spirit lamp, the heat required being somewhat greater than in the reduction of oxides. When hydrochloric acid gas ceases to be disengaged, which is known by fumes ceasing to be produced when a feather or glass rod moistened with ammonia is held near the aperture of the tube, the bulb is allowed to cool and again weighed; the loss of course indicates the amount of chlorine.

(2.) *By fusion with Alkalies.*—The chloride to be analysed (chloride of silver for instance) is mixed in a porcelain crucible with three parts of a mixture of carbonates of potassa and soda, and heated till the mass enters into fusion and effervescence ceases; it is then allowed to cool, and the mass treated with water. The silver remains undissolved in a state of very fine division. It is filtered, washed, ignited, and weighed. The

chlorine in the filtrate, representing that in the compound analysed, is determined as chloride of silver. Gmelin recommends the following process for decomposing chloride of silver:—a crucible is filled almost to the top with an intimate mixture of three parts of the chloride and seven of *colophony;* then exposed to a gentle heat, when the resin burns with a green flame, owing to the hydrochloric acid generated from the chlorine of the chloride and the hydrogen of the resin; a stronger heat is then given to fuse the silver, a little borax is added, and the crucible tapped gently once or twice to facilitate the union of the silver. This process was first proposed by Mohr.

(3.) *By digestion with Caustic Potassa.*—This method is particularly applicable to the analysis of *subchloride of mercury*. The solution filtered from the metallic suboxide is acidulated with nitric acid, and precipitated with nitrate of silver. The suboxide of mercury may be dissolved in aqua-regia, and determined by one of the methods described in section 175; or a fresh portion of the subchloride may be taken and treated with hydrochloric acid and protochloride of tin, as directed p. 369.

Chloride of silver may be decomposed by digestion with caustic potassa; a useful method of preparing pure oxide of silver by this decomposition was proposed by Dr. Gregory (Proc. Chem. Soc. vol. i.). The moist chloride is mixed with a sufficient quantity of caustic potassa, sp. gr. 1·25, and boiled for about ten minutes, or until the chloride has become converted into a jet-black powder. If any white specks be observed, the mixture must be rubbed in a mortar, and again boiled. When the decomposition appears complete, the oxide is to be carefully washed by decantation with hot water until all the saline matter has been removed; it is thus obtained as a heavy black powder. It is worthy of remark, that if the chloride of silver has once been dried, it is only decomposed by boiling for a long time with caustic potassa, and then with great difficulty. According to Dr. Meurer, the above process does not succeed when the experiment is made on several ounces.

Levol modifies the process thus:—he places the chloride in a solution of caustic potassa, in which some *sugar* is dissolved, and then boils. The silver is quickly reduced by the sugar, carbonic acid being evolved, and is brought to the state of fine powder, which is easily washed.

The amount of chlorine in many metallic chlorides may be determined *indirectly* by converting them into sulphates, for

which purpose the compound is treated with concentrated sulphuric acid, and heated till all the hydrochloric acid gas and the excess of sulphuric acid are expelled; the amount of chlorine is inferred from the loss of weight.

Volumetric determination of Chlorine in its combinations.—As a solution of chloride of sodium of known strength may be used to estimate the amount of silver in a fluid, so by adding to a liquid containing hydrochloric acid, or a combination of chlorine with a metal, a solution of silver of known strength, the amount of hydrochloric acid or chlorine may be ascertained. In order to indicate with greater precision the exact point of complete precipitation, Levol employed *phosphate of soda,* which in a neutral liquid indicates the presence of an excess of silver by the production of a yellow precipitate. Mohr (Liebig's 'Annalen,' xcvii.) found that by this means the results are always too high, in consequence of the very light colour of the phosphate of silver, which requires to be present in considerable quantity to become visible in the presence of chloride of silver. *Arsenate of soda* gave better results, but with *chromate of potassa* results of very great accuracy are attainable. If a drop of silver solution be present above the quantity of the chloride, the blood-red colour of chromate of silver makes its appearance distinctly. If 0·2 cubic centimètre too much of the silver solution be added, the mixture is distinctly red. The solution must not be acid, as then chromate of silver is not formed, or only in very small quantities; moreover, bichromate of potassa has a rather red colour. A slight excess of pure carbonate of potassa, on the contrary, is not injurious, because then only the pale yellow colour of chromate of potassa can be exhibited. The standard solution of silver is made by dissolving 108 grains of the pure metal in pure nitric acid, evaporating the solution to perfect dryness on the water-bath, and redissolving the residue in 10,000 grain measures of distilled water. The standard solution of chloride of sodium is made by dissolving 58·5 grains of the pure salt in 10,000 of distilled water. If both solutions have been properly prepared, they will correspond with each other, drop for drop; this, however, must be tested by mixing together equal volumes of the two solutions, shaking the mixture, applying heat, and then allowing the precipitate to subside, the supernatant liquid is decanted, and to one portion of the clear liquid a drop of nitrate of silver is added, and to an-

other a drop of solution of chloride of sodium. Both solutions should remain clear; should however a cloudiness be produced in the portion to which chloride of sodium has been added, it indicates that a small loss has occurred in the evaporation of the silver solution, and its correct strength must be ascertained by repeated experiments; the proportion found forms the basis of the calculations in the determinations of chlorine by the solution. Mohr found by repeated experiments that the excess of the silver solution required to produce a distinct red colour was exactly $\frac{1}{10}$ cubic centimètre, this quantity must therefore be subtracted from the quantity of the silver solution employed. Alkaline chlorides may be determined with great accuracy by this method, which may be employed with concordant results with *urine*, *well water*, *saltpetre*, *potashes*, etc.

Quantitative estimation of free Chlorine.—I. Since chlorine gas is absorbed both by water and mercury, it cannot be estimated by the ordinary methods of measuring gases without very great difficulty. The determination of the gas may be effected by leading it into ammonia, a portion of which it decomposes, chloride of ammonium being formed, and nitrogen gas set free. The operation is conducted as follows:—the substance from which the gas is to be liberated, is introduced into the flask A,

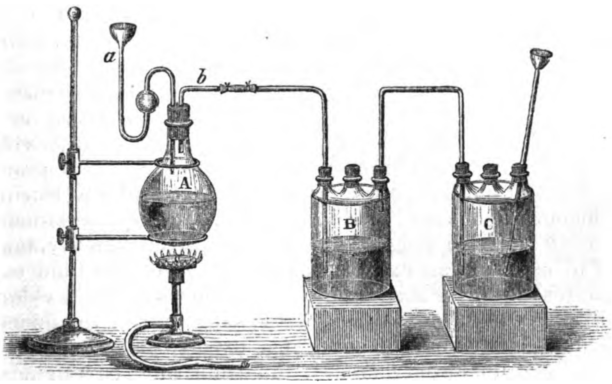


Fig. 83.

Fig. 83. This flask is provided with a well-fitting cork, through which two tubes are inserted, one of which, *b*, communicates

with a Wolfe's bottle, B, containing a sufficient quantity of ammonia to absorb all the chlorine that can be evolved; the other tube, *a*, is a safety-tube, and is surmounted by a funnel, through which any required liquid may be poured into the flask. The Wolfe's bottle, B, is connected with a second bottle, C, also containing ammonia, further to prevent the possibility of any chlorine escaping absorption. This second bottle is provided with a long tube, surmounted by a funnel, in which, during the operation, there is placed some cotton moistened with ammonia. Heat is applied to the flask A, and when the disengagement of chlorine has ceased, all the gas with which the flask is filled, as well as that in the connecting tubes, is expelled, and conducted into the ammonia, by pouring through the funnel of the safety-tube (which during the experiment is filled with a strong solution of common salt) a concentrated solution of bicarbonate of potassa until it is filled. The extremity of the tubes leading from the flask to the first Wolfe's bottle, and from the first Wolfe's bottle to the second, must not quite reach the surface of the ammonia, to avoid the danger of a sudden absorption, and the consequent rushing of the ammonia into the evolution flask. The operation being ended, the ammonia and the moistened cotton are transferred to a beaker, acidulated with nitric acid, and the amount of chlorine condensed, determined by nitrate of silver. The disengagement of the chlorine throughout the experiment must be very slow, otherwise a complete decomposition of the ammonia might not take place, and a portion of chlorine may be liberated in company with the nitrogen. If the chlorine be in aqueous solution, it may be determined by the same decomposition, for which purpose it is only necessary to add excess of ammonia, and then to proceed with the solution in the usual manner. According to Buchner, the amount of chlorine in chlorine water may be determined by agitating it with a weighed amount of metallic mercury, taking care to use such an excess, that a portion of the fluid metal separates in the free state, in order that the whole of the chlorine shall be in the form of the insoluble subchloride; the quantity of chlorine is found by collecting, drying, and weighing the calomel and unaltered mercury, and comparing the weight with that of the metal when introduced into the solution. The same method may be employed to test a solution of chlorine for hydrochloric acid, the chlorine being so entirely removed that the presence of hydrochloric acid may be ascertained by

the acid reaction of the liquid, and its amount determined in the usual manner.

II. Chlorine may also be determined by the use of what is called the *residual method*. The liquid containing it is mixed with a solution containing excess of iodide of potassium, and as soon as the chlorine has been completely absorbed, hyposulphite of soda is added from the burette until the brown colour arising from free iodine has entirely disappeared. Solution of starch paste is then added, and the analysis completed by the addition of the solution of iodine until the blue colour appears. If, then, we note the amount of iodine requisite to produce this reaction, by calculating the equivalent quantity of hyposulphite of soda, and subtracting it from the total amount originally employed, we find by the difference, the quantity of hyposulphite of soda required to saturate the amount of chlorine in the solution. (Scott, 'Handbook of Volumetric Analysis.') (See Iodine.)

III. *Pisani's method* ('Comptes Rendus,' Feb. 16th, 1857).—After the chloride to be analysed has been slightly acidified by pure nitric acid, a known quantity of silver is added to it from a normal solution of nitrate of silver: this should be in slight excess. It is then filtered to separate the chloride of silver, which is carefully washed, the excess of silver is determined in the filtrate, and the difference gives that which is combined with the chlorine, and consequently the chlorine itself. The determination of the silver is effected by means of iodide of starch, which allows the appreciation of a very minute excess of silver employed. The standard solution of iodide of starch is made by preparing a solution of it in water, and ascertaining its strength by its action on a solution of neutral nitrate of silver; upon adding the iodide, the fluid acquires a yellow colour owing to the formation of iodide of silver; the moment the reaction is complete, the fluid becomes bluish-green. A small quantity of pure precipitated carbonate of lime previously added, not only neutralizes any free acid, but enables the operator to hit off with greater exactness the precise time when the reaction is complete.

CHLORIMETRY, OR DETERMINATION OF THE VALUE OF CHLORIDE OF LIME.

(1.) *Modification of the method of Gay-Lussac.*—This is founded on the conversion of calomel into chloride of mercury by the chlorine set free from the bleaching-powder. A fluid is

prepared, holding in suspension a known quantity of subchloride of mercury, into this, a measured quantity of the solution of chloride of lime to be tested is poured, until the liquid becomes perfectly clear; the quantity of chlorine consumed, and consequently the value of the bleaching powder, is calculated from the number of divisions of the burette which have been required to render the turbid mixture clear.

Preparation of the standard Mercurial Test Liquor.—It is based on the following considerations:—

Every 236·5 grains of subchloride of mercury require 35·5 grains of chlorine to convert them into chloride; every 58·5 grains of common salt (which is the chloride most convenient for the purpose) contain 35·5 grains of chlorine, or 164·7 grains contain 100 grains of chlorine.

Let 50 measures of a solution of a subsalt of mercury, the subnitrate, for example, be introduced into the graduated burette, and then poured off into a beaker, and diluted with 4 or 5 ounces of water, then let 82·4 grains of common salt be dissolved in water and introduced into the burette, so as to exactly fill 100 measures. Let this solution be poured gradually into the solution of the subnitrate, (which during the time should be kept warm by immersion in a basin of hot water,) until the last drop added no longer produces a precipitate. Let us suppose that 20 measures have been required; now, as 100 measures of the saline solution contain 82·4 grains of chloride of sodium = 50 grains of chlorine, the 20 measures must contain 16·48 grains = 10 of chlorine. We consequently arrive at the conclusion that 50 measures of the subnitrate of mercury require 10 grains of chlorine to convert the salt into subchloride, and if the 50 measures are increased to 100 by dilution with water a solution is obtained, every 10 divisions of which are equivalent to 1 grain of chlorine, and every single division of which represents $\frac{1}{10}$th of a grain; any quantity of the test liquor may thus be easily prepared.

Method of testing the Bleaching Powder.—100 grains of the specimen, selected from different parts of the sample, and well mixed together, are rubbed in a mortar with a little water, more water is gradually added, the mixture stirred, and the heavier particles allowed to subside; the milky fluid is then poured off, and the precipitate again agitated with water, allowed to stand, and the supernatant fluid poured off, mixed with the first, and transferred to a tube graduated into 200 equal parts, each part

corresponding with a division of the burette; the mortar is rinsed out with a little more water, the washings transferred to the graduated tube, the whole well agitated, and the mark at which the solution stands in the tube is accurately noted. Suppose the whole to occupy 150 measures. The burette is now filled to 100 with the mixture. Next, 100 measures of the standard subnitrate of mercury are poured into a beaker and diluted with water, excess of common salt is added to the solution, which is then acidified with pure hydrochloric acid. The well-agitated solution of chloride of lime is then dropped gradually into the newly-formed calomel in the beaker, until it is perfectly clear, by which it is known that the whole of the calomel has been converted into corrosive sublimate. It must be constantly stirred while the bleaching solution is being added, and it is essential that it should remain acid during the whole time. Now, from what has been explained above, it is evident that the number of divisions of the bleaching solution that have been consumed in rendering the turbid mercurial salt clear, must correspond with 10 grains of chlorine. Suppose 65 measures were required, then the value of the specimen is found very simply by the following proportion:—

$$\text{As } 65 : 10 :: 150 : x,$$

$x = 23{\cdot}07 =$ the quantity of chlorine in 100 grains of the bleaching powder.

It is evident that any other proportions than those here given may be employed, both in making the standard mercurial solution, and in performing the analytical process. The above must be regarded as merely an illustration of the principles of the operation. This method is found to yield very accurate results; there is perhaps one disadvantage attending it, which is, that the solution of subnitrate of mercury is somewhat liable to change, and to give rise to the formation of an insoluble basic salt, which would, of course, interfere with its accuracy.

(2.) *Modification of Gay-Lussac's method by Arsenious Acid.*—When arsenious acid, water, and chlorine are brought into contact with each other, a reaction takes place, the result being the formation of hydrochloric and arsenic acids, thus—

$$AsO_3 + 2HO + 2Cl = AsO_5 + 2HCl.$$

Every equivalent (or 99 parts) of arsenious acid require two equivalents (or 71 parts) of chlorine; consequently 100 parts of chlorine are required to convert 139·45 parts of arsenious acid into arsenic acid. A standard solution of arsenious acid

is prepared by dissolving 139·45 grains of the pure acid in a solution of potassa, diluting the solution, and then adding hydrochloric acid in considerable excess; the volume of the solution is then brought to 10,000 grain measures, and the whole well mixed; every 100 grain measures of the solution thus prepared, contain 1·395 grains of arsenious acid=1 grain of chlorine. When the chlorimetric assay is about to be made, 50 grains of the bleaching powder are prepared in the manner already described, and the burette is filled to the 100th division with the solution; 1000 grain measures of the arsenious acid are then placed in a beaker, diluted with water, and coloured blue by the addition of a few drops of solution of indigo. The bleaching liquid is then gradually and carefully dropped into the arsenical solution, which is all the time well stirred until the blue tinge is entirely destroyed. This shows that the conversion of the arsenious acid into arsenic acid is complete, and consequently that 10 grains of chlorine have been consumed, and as before, the value of the bleaching powder is ascertained by the rule of simple proportion: thus, supposing 90 measures have been consumed, then—

$$\text{As } 90 : 10 :: 100 : x,$$

$x = 11{\cdot}11 =$ the quantity of chlorine in 50 grains of the bleaching powder, or 22·22 per cent.; or still more simply, as each measure of the burette corresponds with half a grain of bleaching powder, and as the number of measures consumed contain 10 grains of chlorine, we find at once the percentage amount of chlorine, by dividing 2000 by the number of measures required; thus:—

$$\frac{2000}{90} = 22{\cdot}22.$$

(3.) *Otto's method by Protosulphate of Iron.*—When protosulphate of iron, water, chlorine, and free sulphuric acid are brought into contact, a reaction takes place, resulting in the formation of hydrochloric acid and persulphate of iron; thus:—

$$2(FeO,SO_3) + HO,SO_3 + Cl = (Fe_2O_3,3SO_3) + HCl.$$

every two equivalents, or 152 parts of anhydrous, or 278 parts of crystallized protosulphate of iron, require one equivalent, or 35·5 parts of chlorine; 100 grains of chlorine are therefore required to convert 783·1 grains of crystallized protosulphate of iron into persulphate. To prepare the iron salt for these experiments, Fresenius directs that iron nails free from rust be dissolved in dilute sulphuric acid, finally with the applica-

tion of heat; the solution is filtered while still warm, into about twice its volume of spirits of wine; the precipitate which is produced consists of protosulphate of iron with seven equivalents of water. It is collected on a filter, edulcorated with spirits of wine, spread upon a sheet of blotting-paper, and allowed to dry in the air until it has completely lost the smell of spirits of wine: the dry salt must be kept in a well-closed bottle. To perform the chlorimetric assay, 78·3 grains of the protosulphate are dissolved in about two ounces of water, and the solution strongly acidulated with sulphuric acid; 50 grains of the bleaching-powder are then prepared as before directed, and the burette filled with the solution, which, after being well agitated, is added drop by drop to the solution of the iron salt until complete peroxidation has taken place; this is known by solution of red prussiate of potassa no longer striking a blue precipitate. The best way of testing the solution from time to time, is to cover a large white plate with drops of the red precipitate, and, as the operation draws towards an end, to convey a minute drop from the solution, at the end of a small stirring-rod, to one of the drops; the process is complete when prussian blue ceases to be formed, a green colour being produced in its stead. The number of divisions of the burette which have been consumed is now noted; this corresponds with 10 grains of chlorine, that being the quantity required for the peroxidation of 78·3 grains of crystallized protosulphate of iron. The calculation is precisely the same as in the last method.

(4.) *By Yellow Prussiate of Potash.*—When ferrocyanide of potassium is brought into contact with free chlorine, a reaction takes place, resulting in the production of *ferricyanide* of potassium and chloride of potassium; thus:—

$$2(K_2Cfy)+Cl=K_3Cfy_2+KCl.$$

Every two equivalents, or 368 parts of anhydrous, or 422 parts of crystallized ferrocyanide of potassium require one equivalent, or 35·5 parts of chlorine; 100 grains of chlorine, therefore, are required to convert 1188·7 grains of crystallized yellow prussiate of potassa into red prussiate, or 118·87 grains correspond to 10 grains of chlorine. The experiment is conducted in precisely the same manner as before, and as soon as the whole of the ferrocyanide is converted into ferricyanide, the mixture ceases to give prussian blue with a solution of peroxide of iron.

IODINE.

199. Hydriodic Acid.

I. *Estimation as Iodide of Silver.*—Iodine when present in a solution in the form of hydriodic acid, and in the absence of bromine and chlorine, is best precipitated in the form of iodide of silver, by solution of nitrate of silver. This salt, which when newly precipitated is of a pale yellow colour, has many properties in common with the corresponding chlorine and bromine compounds. Thus, it is insoluble in water and in dilute nitric acid, and soluble, though with difficulty, in ammonia.* Like bromide of silver, it is decomposed by chlorine; it also blackens when exposed to the light, and, when heated, it fuses into a horny mass, without undergoing decomposition. Its composition is—

One equivalent of I . . .	127 . .	54·04
One ditto of Ag . .	108 . .	45·96
One ditto of AgI . .	235 . .	100·00

II. *Estimation as Protiodide of Palladium.*—In the presence of hydrobromic and hydrochloric acids, iodine may be very accurately estimated in the form of *protiodide of palladium*, by means of protochloride of palladium. The precipitate, which is of a deep brown-black colour, is allowed to settle for some hours; it is then collected on a tared filter, dried at a temperature below the boiling-point of water, or, what is still better, *in vacuo*, over sulphuric acid, and weighed. Its composition is—

One equivalent of I . .	126·36 . .	70·34
One ditto of Pd . .	53·27 . .	29·66
One ditto of PdI . .	179·63 . .	100·00

III. *Estimation as Protiodide of Copper.*—Iodide may also be estimated by the process recommended by M. Duflos, viz. by precipitating it in the form of protiodide of copper by a solution of sulphate of copper in concentrated sulphurous acid; the precipitate may either be collected on a filter, washed, and determined as protiodide of copper, or it may be dissolved in dilute nitric acid, precipitated by nitrate of

* According to Wallace and Lamont (Chem. Gaz., vol. xvii. p. 140) 1 part of iodide of silver is soluble in 2793 parts (measure) of liquid ammonia, sp. gr. ·890, and 1 part of chloride of silver in 12·38 parts of the same solution.

silver, and weighed as iodide of silver. This method is well adapted to the separation of iodine from chlorine, in cases where the presence of chlorine is immaterial. M. Sarphati (Ann. der Chem. und Pharm., xxxix. p. 254) recommends a solution of chloride of copper in dilute hydrochloric acid; or a solution composed of 1 part of crystallized sulphate of copper, and 1½ of crystallized sulphate of iron.

IV. *Pisani's method.*—Iodine, in alkaline iodides, may also be estimated by the following method, recommended by Pisani ('Comptés Rendus,' February 16, 1857):—A few drops of soluble iodide of starch are added to the liquid containing the iodide to be analysed: the quantity must be sufficient to give it a distinct blue tint. A normal solution of silver is then dropped in until the iodide of starch is decolorized, which only takes place after the complete precipitation of all the iodine contained in the alkaline iodide. The number of divisions employed is then read off, and the corresponding quantity of iodine calculated.

V. *Indirect method.*—Iodine is sometimes determined by the *indirect* method, viz. by converting the base or bases with which it is combined into sulphates, by digestion with sulphuric acid in a porcelain capsule, and calculating the quantity of iodine from the loss. Metallic iodides, which are insoluble in water, may be decomposed by ignition with carbonate of soda; iodide of sodium is obtained on treating the fused mass with water, from which the iodine may subsequently be precipitated by nitrate of silver. The base or bases are found in the insoluble residue, either as carbonates or oxides. Metallic iodides may also be decomposed by boiling with caustic potassa.

VI. *Estimation of free Iodine.*—Iodine in a free state, in aqueous solution, cannot be determined in the same manner as chlorine and bromine, viz. by the decomposition of ammonia, since the contact of iodine with ammonia gives rise to the formation of iodide of nitrogen, which is not decomposed by excess of ammonia. In order to estimate the iodine under these circumstances, it may be dissolved in excess of caustic potassa, the solution, which must be colourless, treated with nitric acid, and precipitated by nitrate of silver; the washed and dried precipitate is ignited, by which the small quantity of iodate of silver formed, is converted into iodide.

Separation of Iodine from Chlorine.—Of all the methods which have been proposed, none are so convenient or easy of

execution as that of precipitating the iodine in the form of protiodide of palladium by protonitrate of palladium. The separation is complete, and the chlorine in the filtrate may be precipitated by nitrate of silver, after having removed the excess of palladium by sulphuretted hydrogen, and afterwards destroying the excess of the latter by a solution of sulphate of sesquioxide of iron. It is better however to operate on two different portions of the solution, determining the iodine in one by protochloride of palladium, and precipitating the chlorine and iodine together in the other by nitrate of silver; from the weight of the precipitate is subtracted that of the iodide of silver corresponding with the quantity of iodide of palladium found.

Estimation of Iodine in Kelp.—The following process has been employed by Wallace and Lamont (Chem. Gaz., vol. xvii. p. 137). It is based upon two well-established facts,—1. that when nitrate of silver is added to a solution containing iodine and chlorine, the iodine is thrown down first; and 2. that iodide of silver is only sparingly soluble in liquid ammonia, while chloride of silver is freely soluble in that liquid. 500 grains of the pulverized and well-mixed sample are boiled with water, and the liquor and washings are nearly but not quite neutralized with nitric acid, and evaporated to a small bulk. The residue is then fused by the application of a stronger heat, and kept in this condition for a few minutes, when all the sulphur compounds are converted into sulphates without danger of decomposing the iodide. The fused mass is dissolved in water, the solution filtered (if necessary), and nitrate of silver added in small successive portions with brisk agitation, until the precipitate produced on a further addition is perfectly colourless; nitric acid is now added in excess, and the mixture is well washed by decantation. The last washing is decanted as completely as possible, half an ounce of the strongest liquid ammonia is added, and the mixture vigorously shaken. The digestion is continued for several hours, after which the iodide of silver is collected on a small tared filter, and washed first with liquid ammonia, and subsequently with hot water, it is then dried. The weight of the iodide of silver + ·1 grain (dissolved by the ammonia) divided by 5 and multiplied by ·54, gives the percentage amount of iodine in the sample.

A method of detecting the presence of iodine in waters has been proposed by S. de Luca ('Comptes Rendus,' Aug. 1,

1859). It is founded on the power possessed by bromine of decomposing iodides, and setting free iodine. The water is precipitated by nitrate of silver, the precipitate, washed and dried, is placed at the bottom of a glass tube, and on it is dropped a small glass bubble filled with vapour of bromine. The air in the tube is replaced by carbonic acid, and the tube is then hermetically sealed. By shaking the tube two or three times the little bubble is broken, when the vapour of bromine comes in contact with the iodide, which it decomposes, setting free iodine in the form of violet fumes, which condense on the cold part of the tube, and may be dissolved out by alcohol. The amount of iodine may be estimated by a standard solution of sulphurous acid, and the hydriodic acid may afterwards be reconverted into iodide of silver, and weighed.

Another method has been employed by MM. O. Henry and Humbert ('Comptes Rendus,' March 23, 1857). The precipitate by nitrate of silver is washed and dried; it is then mixed intimately with *cyanide* of silver, and introduced into a tube, at one end of which it is fixed between two plugs of asbestos. A current of very dry chlorine is then passed slowly over the mixture, whilst the tube is slightly heated. The iodine and cyanogen are displaced, combine, and condense in the colder parts of the tube, in the form of a white crystalline ring of iodide of cyanogen.

To detect iodine in the presence of nitric acid Stein (Polyt. Centralbl., 1858) employs *tin* as a reducing agent and bisulphide of carbon as a solvent for the iodine. A quantity of the acid to be tested is poured into a test tube, and a rod of tin immersed in it until red fumes are distinctly evolved. The rod of tin is then taken out, and a small quantity of sulphide of carbon added to the liquid, the mixture is shaken and left quiet for a few moments. The stratum of sulphide of carbon which usually collects over the acid appears of a red colour, unless the amount of iodine be too small. With traces of iodine, the colour is only deep yellow. In this case however, it becomes red, when the sulphide of carbon is drawn off and evaporated in a small porcelain capsule by blowing upon it.

It was discovered by Dupasquier that when iodine and sulphurous acid are brought into contact, in the presence of water, sulphuric and hydriodic acids are formed thus:—

$$I + HO + SO_2 = HI + SO_3$$

and on this he founded a volumetric process for the estimation

of iodine. Bunsen found the results unsatisfactory in consequence of a reverse action which ensues when the sulphurous acid is present beyond a certain quantity thus :—

$$HI + SO_3 = I + HO + SO_2.$$

He ascertained, however, that the former reaction alone takes place if the quantity of sulphurous acid does not exceed from 0·04 to 0·05 per cent. of anhydrous acid, and that under these circumstances one equivalent of iodine converts one equivalent of sulphurous acid into sulphuric acid; on this he has based a volumetric method applicable to a great number of analytical operations depending on oxidation and reduction, the oxidizing substance being iodine. For details of his process we must refer to the author's original memoir (Annal. der Chem. und Pharm. 86, 265),* or to works specially devoted to volumetric analysis (Scott, Sutton).

BROMINE.

200. Hydrobromic Acid.

When present in a solution in the form of hydrobromic acid, bromine is determined by precipitating it in the form of bromide of silver, precisely in the same manner as chlorine. Like the chloride, the bromide of silver is insoluble in water and in nitric acid: it is yellowish-white when precipitated, but it changes colour when exposed to the light. It is decomposed by chlorine, bromine being separated. When heated, it fuses, solidifying, on cooling, into a yellow horny mass. Its composition is—

One equivalent of Br	80·0 . .	42·55
One ditto of Ag	108·0 . .	57·45
One ditto of AgBr . . .	188·0 . .	10·00

The analysis of bromides may be effected in the same manner as that of the corresponding chlorides. The indirect method is, in many cases, the most convenient: a weighed quantity of the compound is decomposed by heating it in a porcelain capsule, with concentrated sulphuric acid; the amount of metal is calculated from the weight of the resulting sulphate, and that of the bromine from the loss sustained. The analysis of those bromides, the bases of which are capable of being precipitated by sulphuretted hydrogen, may be performed by that

* Translated in full in the Journal of the Chemical Society, vol. viii. p. 219.

reagent. Free bromine, in aqueous solution, is determined in exactly the same manner as free chlorine.

Separation of Bromine from Chlorine.

Two methods of performing this analysis are known, a *direct* and an *indirect* method.

I. *Direct method.*—This is based on the solubility of bromide of barium in absolute alcohol, and the insolubility of chloride of barium in the same menstruum. The two substances are precipitated together out of their solution, by nitrate of silver; the precipitates, after having been washed and dried, are reduced by being brought into contact with zinc and dilute sulphuric acid, there are thus formed bromide and chloride of zinc, which are dissolved in the acid liquor; on the addition of excess of baryta water, the zinc is precipitated together with sulphate of baryta in the form of hydrated oxide; the filtered solution contains bromide and chloride of barium, it is evaporated to dryness, and the dry mass treated with absolute alcohol, which, as above stated, dissolves only the bromide of barium. The bromine is separated from the barium in the alcoholic solution, and the chlorine from the barium in the solution obtained on treating the residual mass with water, by one of the methods already given. This method does not give absolutely accurate results.

II. *Indirect method.*—This is based on the decomposition of bromide of silver by chlorine gas. The bromine and chlorine are, as before, precipitated together, by a solution of nitrate of silver, and the precipitate having been washed, dried, fused, and very accurately weighed, is introduced into a bulbed tube of hard glass, the exact weight of which has also been noted. The tube is connected with an apparatus for evolving chlorine, and a current of that gas dried by passing through chloride of calcium, is caused to traverse the tube, to which heat is at the same time applied sufficient to keep the mixed silver salts in a state of fusion. After the operation has been continued for about half an hour, the tube is allowed to cool, and the chlorine in its interior having been replaced by atmospheric air, it is again weighed; the process is again repeated, and the tube a second time weighed: should the second weight correspond with the first, the analysis is complete; if not, the process must be again repeated, till the two last weighings are absolutely alike.

The amount of bromine originally present is calculated from

the diminution in the weight of the mixture, the bromide of silver being now replaced by chloride of silver. The calculation is made thus :—Suppose the weight of the mixed chloride and bromide to have been 100 grains, and, after the experiment, suppose the weight to have decreased 5 grains. The equivalent of bromide of silver is 188·0, that of chloride of silver 143·5; then, as 44·5 (the difference between the respective equivalents of bromide and chloride of silver) : 188·0 (the equivalent of bromide of silver) :: 5 (the difference in weight found in the experiment) : x. $x = 2{\cdot}112 =$ the quantity of bromide of silver in the mixture analysed.

Separation of Chlorine, Bromine, and Iodine.

I. Pisani's method ('Comptes Rendus,' Feb. 16, 1857). The liquid is divided into two parts, to one of which a known slight excess of silver is added, the precipitate is filtered, washed, and weighed, and the excess of silver in the filtrate is determined by iodide of starch. The difference gives the quantity of silver combined with the chlorine, bromine, and iodine. From the other portion of the liquid the iodine is precipitated by nitrate of palladium; it is filtered and estimated, and the weight of the silver salt which it would form being deducted from the joint weights of chloride, iodide, and bromide of silver found, the difference gives the joint weights of the bromide and chloride of silver, from which the quantity of silver being known, the weights of the chlorine and bromine in the mixture are calculated.

II. Lyte and Field's method (Quart. Journ. Chem. Soc., vol. x. p. 234).—This is founded on the fact that chloride of silver is decomposed by bromide of potassium, and both chloride and bromide of silver by iodide of potassium. When a mixed solution of bromide of potassium and chloride of sodium is added gradually to a solution of nitrate of silver not in excess, no trace of chloride of silver is precipitated as long as any bromide remains in solution. If, to a similar solution, iodide and bromide of potassium and chloride of sodium be added, iodide of silver and nitrate of potassa are formed, bromide of potassium and chloride of sodium remaining undecomposed; when bromide of potassium is poured upon chloride of silver, an entire decomposition ensues, bromide of silver and chloride of potassium being produced. When iodide of potassium is added to chloride of silver, iodide of silver and chloride of potassium

are formed; and when iodide of potassium is added to bromide of silver there is a similar decomposition, the iodine replacing the bromine. When chloride of silver in excess is agitated with a solution of iodide of potassium, and warmed for some hours, no trace of iodine can be detected in the solution; when however chloride of sodium is poured upon iodide of silver, no decomposition occurs, neither is there any action upon bromide of silver with the same salt: and when bromide of potassium is added to iodide of silver, there is no alteration in the union of the elements. Hence the following simple method of analysing a mixture containing bromides, iodides, and chlorides.

The liquid is divided into three portions. To the first is added slight excess of nitrate of silver, and the precipitate with the requisite analytical precautions, is weighed. To the second is added nitrate of silver as before, the precipitate is filtered off, washed, returned to the flask and digested in a weak solution of bromide of potassium. A similar operation is performed upon the third, the precipitate in this instance however being digested with a weak solution of iodide of potassium instead of bromide. In the first precipitate, we obtain the combined weights of the chloride, iodide, and bromide of silver; in the second the combined weights of the bromide and iodide of silver, and in the third, that simply of the iodide of silver. Bromide of potassium having no action upon iodide of silver has converted the chloride into bromide, leaving the iodide untouched; while iodide of potassium having the power to decompose both chloride and bromide, the whole is converted into the iodide. The calculation is very simple: as the difference between the equivalents of bromide of silver and chloride of silver (44·5) is to the equivalent of chloride of silver (143·6), so is the difference in weight after digesting in bromide of potassium to the quantity of chloride of silver originally present; and as the difference of the equivalents of bromide and iodide of silver (47·1) is to the equivalent of bromide of silver (188), so is the excess in weight of the precipitate after digestion in iodide of potassium to the weight of bromide of silver originally present. Fresenius ('Quantitative Analysis,' Eng. Trans. p. 393) objects to this method, which he says may give rise to very considerable mistakes, on account of the solubility of iodide of silver in iodide of potassium solution, and of bromide of silver in bromide of potassium solution. Field has however shown (Chem. News, vol. ii. p. 324) that there is no force in this objection,

provided the solutions of the solvents, iodide and bromide of potassium, be sufficiently weak; and that if this be carefully attended to, the results are reliable.

CYANOGEN.

201. Hydrocyanic Acid.

This acid, when in a free state, is best estimated by precipitating it in the form of cyanide of silver. It falls as a white curdy mass, which is insoluble in water, and in dilute nitric acid, but soluble in ammonia. Unlike the chloride, bromide, and iodide of silver, it does not change colour when exposed to light, neither will it bear ignition without being decomposed. It may, however, be dried at 212°, without alteration. For its composition, see page 353. Soluble cyanides may also be precipitated by nitrate of silver; insoluble cyanides, which do not readily dissolve in dilute nitric acid, may be analysed by determining the amount of carbon and nitrogen which they contain by the methods of organic elementary analysis; or the amount of cyanogen may be determined in the indirect manner, by igniting the compound, and weighing the residue. According to Rose (Poggendorff's 'Annalen') it is better to treat the compound with concentrated sulphuric acid and a little water, and to heat the mixture long enough to get rid of nearly all the excess of sulphuric acid. All cyanides, simple and double, even cyanide of silver, as well as nitro-prusside of sodium and the sulpho-cyanides, are transformed by this process into sulphates, which present no difficulty in analysis.

Double cyanides containing metals whose cyanides are soluble in nitric acid,—those of *nickel*, *copper*, and *zinc*, for instance,—may be analysed thus:—Cover the solid cyanide with a solution of nitrate of silver, and then with water, and a certain quantity of nitric acid, taking care not to add too large an excess, cyanide of silver being more soluble in nitric acid than chloride. Weigh the cyanide of silver dried at 212° on a weighed filter, or, still better, calcine it at a moderate temperature so as to avoid melting the silver until it ceases to lose weight.

The cyanogen in mercuric cyanide cannot be precipitated in the form of cyanide of silver, a crystalline compound of nitrate with cyanide being formed, which is soluble in water. For analysing this salt, Rose dissolves it in twenty-five or thirty times its weight of water, and leaves the solution for thirty-six

hours in contact with an equal weight of cadmium filings in a well-stoppered bottle; he then adds nitric acid and nitrate of silver, and obtains almost the theoretical quantity of cyanide of silver.

A large number of simple and compound cyanides are easily transformed into cyanide of mercury by boiling them with excess of oxide of mercury; the metal of the cyanide separates in the state of oxide, and the cyanogen combines with the mercury. Smith proposes to decompose and estimate hydrocyanic acid by means of chloride of lime, a process which occupies but a few seconds; the products are nitrogen gas and carbonate of lime.. In some cases he prefers the employment of chloride of soda to chloride of lime, on account of the solubility of the compounds that are formed. The same method is applicable to the analysis of the salts of cyanogen, and also to that of the ferrocyanides.

The usual method of analysing the latter, when free from alkali, is to fuse them, in small portions at a time, at an intense heat, in a porcelain crucible, with nitre. The bases which remain are separated from each other by the ordinary processes, and the cyanogen is estimated in a fresh portion by the direct determination of the carbon and nitrogen. Alkaline ferrocyanides are decomposed by boiling sulphuric acid, nitric acid, or aqua-regia, and the evaporated mass treated as usual for the bases. The reason why it is inadmissible to decompose them by fusion with nitre is, that an explosion would certainly result from the contact of the nitre with the fused salt. Those alkaline double cyanides, which resist decomposition by boiling concentrated acids, are kept for a long time ignited in the air, or in contact with oxide of copper; and, should the ferrocyanide under examination contain a volatile metal, the latter must be determined by dissolving a separate portion of the compound in caustic potassa, or in hydrochloric acid, and precipitating the metal with sulphuretted hydrogen.

A method of analysing compounds of cyanogen, founded on the action of *iodine*, has been proposed by M. V. Gerdy ('Comptes Rendus,' Jan. 22, 1842). It was found by this chemist that in many of the soluble combinations of cyanides, the cyanogen may be substituted, atom for atom, by iodine; so that, from the amount of solution of iodine employed and decolorized before its action on starch becomes evident, it is possible to calculate with the greatest ease, and in a few moments,

the amount of the cyanogen contained in the liquid, and the quantity of metal with which it was combined. Gerdy has thus analysed cyanide of potassium with great accuracy. He states, also, that the method is equally applicable to the analysis of cyanide of mercury; of the double compound of cyanide of potassium and cyanide of silver, which contains eight atoms of cyanogen to one of silver; of cyanide of silver, dissolved in ferrocyanide of potassium; of double cyanide of potassium and copper; of cyanide of gold dissolved in cyanide of potassium, etc. The analysis of cyanide of gold is, he says, not so easy of execution, according to this method, as is the case with the other compounds above mentioned, and requires some care. The reaction is here of a different description; for, while eight atoms of cyanogen are required to dissolve one atom of gold, viz. four atoms combined with the gold, and four with the potassium, four atoms of iodine alone suffice to effect the decomposition. This peculiarity he considers to be owing to the cyanide of gold not being acted on by the iodine, and being only precipitated entirely when the iodine has decomposed the whole of the cyanide of potassium.

Determination of the amount of Hydrocyanic Acid in the medicinal Hydrocyanic Acid, Bitter Almond, and Cherry-Laurel waters (Liebig).—This process is founded on the fact that oxide and chloride of silver are soluble in cyanide of potassium up to a certain point, viz. until the double compound consisting of equal equivalents of cyanide of potassium and cyanide of silver is formed, which compound is not decomposed by excess of potash. To the liquid containing the prussic acid, caustic potassa is added until it has a strong alkaline reaction, and then a few drops of chloride of sodium. A solution of nitrate of silver of known strength is then added, drop by drop, from a burette until a slight milkiness is perceptible. The quantity used is noted; every equivalent of silver consumed exactly corresponds to two equivalents of prussic acid. The presence of formic or hydrochloric acid has no influence on the result. The method may be employed advantageously to test the purity of commercial cyanide of potassium. (Liebig's Annalen, Jan. 1851.)

Separation of Cyanogen from Chlorine, Bromine, and Iodine.—The best method is to precipitate all three of the electronegative elements with nitrate of silver, and, having carefully collected, washed and dried the precipitate in the water-bath, to determine the amount of carbon and nitrogen yielded by the

mixture by the ordinary methods of organic analysis. From the numbers obtained, the amount of cyanide of silver is calculated, and the proportion of iodine, bromine, and chlorine is inferred from the difference.

Fresenius gives the following method of determining the relative proportions of hydrocyanic and hydrochloric acids, when together present in a solution. It is founded on the circumstance, that percyanide of mercury is not decomposed by nitrate of silver. The solution is divided into two equal parts. One portion is precipitated with nitrate of silver, and the mixed precipitate of chloride and cyanide of silver weighed; the other portion is mixed with oxide of mercury, and the mixture agitated until perfectly inodorous. The fluid is then filtered off, the filtrate subsequently precipitated with nitrate of silver, and the precipitate weighed. The difference between the respective weights of the two precipitates indicates the amount of cyanide of silver contained in the precipitate in the first portion.

FLUORINE.

202. Hydrofluoric Acid.

When this acid exists in aqueous solution, it is quantitatively estimated by rendering the liquid alkaline by ammonia, and precipitating the hydrofluoric acid in the form of fluoride of calcium by the addition of chloride of calcium; the precipitate, which is gelatinous, is washed on the filter with hot distilled water, and then with acetic acid, to remove any carbonate of lime which may have formed during the process of filtration. The composition of the ignited salt is—

One equivalent of Ca . . .	20 . .	51·28
One ditto of Fl . . .	19 . .	48·72
One ditto of CaFl . .	39 . .	100·00

The fluorine in soluble fluorides may be determined in the same manner, the bases being estimated in the filtrate according to the usual rules. To detect fluorine in water, Mené treats the solid residue of a large quantity of the water with an excess of concentrated sulphuric acid, and passes the gaseous products into water slightly ammoniated, in which, if fluorine were present in the water, some gelatinous silica is obtained, from the decomposition of the fluoride of silicon which was disengaged from the residue.

Insoluble fluorides may be analysed in two ways.

(1.) *Decomposition by Sulphuric Acid.*—The fluorine in this process is estimated *indirectly*. A weighed quantity of the fluoride, finely pulverized, is heated in a platinum capsule with concentrated sulphuric acid; the fluorine escapes in the form of hydrofluoric acid gas, and the excess of sulphuric acid is finally expelled by raising the heat to ignition. From the weight of the resulting sulphate, the quantity of metal in the base is calculated; that of the fluorine is indicated by the loss of weight. Should the substance analysed contain more than one base, the resulting sulphates must be submitted to further analysis, before a calculation can be made of the amount of fluorine present in the substance.

(2.) *Conversion of the Fluorine into Fluoride of Silicon*, Wöhler's process (Poggendorff's 'Annalen,' vol. xlviii.).—The weighed substance is intimately mixed with pure silica, unless it already contains some; the mixture is placed in a small flask which can be weighed on the balance; very concentrated sulphuric acid, which has been boiled, is added, and the flask quickly closed with a cork, through which a small tube, filled with fused chloride of calcium, and drawn out to a fine point, passes. The whole apparatus is now weighed, and then exposed to a proper heat, as long as gaseous fluoride of silicon is evolved. The last portions are removed by exhaustion under the air-pump. The loss of weight which it experiences is fluoride of silicon, from which the amount of fluorine is calculated. 1·395 parts of fluoride of silicon are formed for each part of fluorine. To test this method, the author estimated the amount of fluorine in fluorspar, and the results were accurate to the first decimal place. To avoid the use of the air-pump, Fresenius modifies the apparatus by adding a second tube, closed with a wax stopper, the lower end reaching nearly to the bottom of the flask; the last traces of gas may, with this arrangement, be removed from the flask by simple suction: for which purpose a suction tube is applied, filled with dry cotton at the lower end, and with moist cotton in the centre. The above process is well adapted for the separation of fluorine from the silicates. Another method, proposed by Berzelius and modified by Regnault, is the following:—the finely levigated powder is kept for some time in a state of fusion, with four times its weight of carbonate of soda; it is then extracted with boiling water, and the filtered solution is mixed with a solution

of carbonate of zinc in ammonia, and evaporated to dryness. By digesting the dry residue with boiling water, a solution is obtained, which contains the whole of the fluorine in the form of fluoride of sodium, in conjunction with carbonate of soda. It is carefully neutralized with hydrochloric acid, and the carbonic acid completely removed by allowing it to stand for some hours under a bell jar, by the side of a vessel containing solution of caustic potassa. The hydrofluoric acid is finally precipitated and estimated in the form of fluoride of calcium.

Where the fluoride to be analysed contains water, the amount of that substance cannot be estimated by simply heating the fluoride, since the simultaneous action of the air and the water sometimes effects a partial decomposition of the fluoride, and a portion of hydrofluoric gas escapes along with the vapour of water. In such cases the analysis is performed as follows:—The joint amount of water and fluoride is first determined by heating a known weight of the substance with concentrated sulphuric acid in the manner above described; a fresh portion of the compound is then mixed in a little glass retort with about six times its weight of finely pulverized and recently ignited protoxide of lead; the mixture is covered with a layer of oxide of lead, the retort is weighed, and heat is then applied, gentle at first, but gradually increasing to redness; aqueous vapour, unaccompanied with the slightest trace of hydrofluoric acid gas, escapes. The retort is allowed to cool; it is then weighed again, and the amount of water calculated from the loss which it has sustained. By the first operation the joint amount of water and fluorine has been learnt; and we have only now to deduct from that amount the quantity of water, indicated by the second experiment, to find the quantity of fluorine in the substance under examination.

Separation of Fluorides from Phosphates.—The process of Berzelius as modified by Regnault, which we have described above, for separating fluorides from silicates, may also be employed when phosphates also are present. In this case the solution filtered from the silicic acid will contain phosphate of soda in addition to fluoride of sodium and carbonate of soda. It is analysed as follows:—it is rendered ammoniacal, and mixed in a glass flask which can be closed air-tight with a solution of chloride of calcium; the precipitate which is produced consists of fluoride of calcium and phosphate of lime. It is washed with the proper precautions, dried, ignited, and weighed; it is

then treated in a platinum crucible with concentrated sulphuric acid, and heated until the whole of the hydrofluoric acid is expelled. The residue is treated with alcohol, in which sulphate of lime is insoluble, and the phosphoric acid dissolved in the alcohol is precipitated and estimated as pyrophosphate of magnesia. The amount of fluorine originally present in the mixed precipitate of fluoride of calcium and phosphate of soda, is learnt by the loss of weight sustained by the action of the sulphuric acid.

203. Nitric Acid.

(1.) *Estimation of free Nitric Acid by Hydrate of Baryta.*—If nitric acid exist in a solution in a free state, baryta-water may be added until the liquid begins to acquire a slightly alkaline reaction: the whole is then evaporated to dryness. The dry mass is dissolved in water, and the carbonate of baryta which may have been formed during the evaporation, having been removed by filtration, dilute sulphuric acid is added. The quantity of nitrate of baryta is calculated from the weight of the sulphate precipitated, and from this is deduced the weight of the nitric acid originally present in the solution. Care must be taken not to add the baryta-water in too great excess.

According to Schaffgotsch (Poggendorff's 'Annalen,' cviii. p. 64), free nitric acid may be estimated in the form of nitrate of ammonia, a salt of perfectly constant composition, which can be easily weighed in a covered crucible, after being dried at 240° F.

(2.) *By the process of Acidimetry.*—This method, which is based on the determination of the amount of carbonic acid expelled by a weighed quantity of the acid under examination, is best performed with the alkalimetrical apparatus of Fresenius and Will (see annexed figure). It being indispensable that the bicarbonate employed for this experiment should be entirely free from neutral or sesquicarbonate (though its perfect freedom from any admixture of sulphate and chloride is not of consequence) Fresenius and Will recommend to purify the bicarbonate of soda of commerce in the following manner:—Half a pound or a pound is reduced to a uniform powder, and a portion of it first tested with bichloride of mercury; if the solution becomes merely turbid or milky at first, it is tolerably free from carbonates, the powder is then put into a glass jar and covered with the same amount of cold rain-water; it is

allowed to stand for twenty-four hours, with frequent stirring. The salt is then placed upon a funnel, the tube of which is stopped with loose cotton, so as to allow the ley to drop off. The salt is then washed several times with small quantities of cold rain-water; what remains is generally pure, and adapted for acidimetrical purposes. It is dried between some sheets of blotting-paper, without the aid of heat, and kept for use in a well-closed glass jar. The operation is conducted as follows:—A portion of the fluid to be examined is carefully weighed into *b*; if the acid be concentrated, from four to eight times its amount of water should be added. A little glass tube is provided, capable of holding about 75 grains of bicarbonate of soda; it is filled nearly to the brim with the alkali, and, a silk thread being tied round its upper end, it is lowered down into *b*, so as to remain suspended perpendicularly when the flask is closed, the silk thread becoming fixed between the cork and the glass. The apparatus is then arranged as described (page 269), and accurately weighed. When the operation is about to be commenced, the cork of the flask *b* is slightly loosened, so as to allow the little tube, together with its silk thread, to fall into the acid, and immediately fixed again air-tight. The evolution of carbonic acid commences instantaneously, and continues in a uniform and uninterrupted manner till the acid is completely neutralized. The operation may be accelerated by repeatedly shaking the apparatus. When no more bubbles of gas appear upon agitation, the flask *b* is placed up to its neck in hot water, and there left until the renewed evolution of gas has completely ceased; this is also promoted by agitating the apparatus. The wax stopper is then removed from *d*; the flask removed from the hot water, wiped dry, and suction applied to *e* until the carbonic acid is completely removed. The apparatus is allowed to cool, and again weighed; the amount of anhydrous acid in the sample examined is determined from

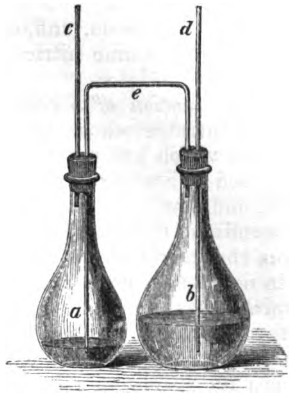


Fig. 84.

the amount of carbonic acid evolved; every two equivalents of the latter indicate one equivalent of nitric acid. It is evident that this method applies to all acids capable of decomposing bicarbonate of soda, and, consequently, that it cannot be employed to determine nitric acid in the presence of any other free acid.

Determination of Nitric Acid in combination with bases.— Those nitrates whose bases form with sulphuric acid compounds which are not decomposed by mere ignition, may be analysed by heating them in a platinum crucible with sulphuric acid, and, having expelled the excess of acid by feeble ignition, determining the quantity of nitric acid expelled, by calculation from the weight of the sulphate obtained. Nitrates which contain no water of crystallization, may also be analysed by simple ignition, nothing but pure metallic oxide being in most cases left; the amount of nitric acid is inferred from the loss of weight. If the salt to be examined be mixed with two or three times its weight of perfectly anhydrous *borax*, the decomposition is effected at a lower temperature, and without danger of deflagration. A still better method is to fuse the alkaline nitrate to a dull red-heat with 2½ times its weight of *bichromate of potassa:* neither chlorides nor sulphates are under these conditions decomposed. Hydrated nitrates are analysed by determining the base in one portion, and the water and nitric acid in another, by the method of organic elementary analysis. Nitrates, the bases of which are precipitable by sulphuretted hydrogen, may be analysed by removing the base by that reagent, excess of which should be avoided, and determining the amount of nitric acid in the filtrate by hydrate of baryta, in the manner described at the beginning of this section.

The analysis of those nitrates which are insoluble in water may be effected also by sulphuretted hydrogen. They should be reduced to a state of minute division, and kept suspended in water while a stream of sulphuretted hydrogen is passed through the liquid.

From *baryta, strontia,* and *lime,* nitric acid may be separated by mixing the solution with slight excess of sulphuric acid; and, in the case of *lime* and *strontia,* adding also alcohol, to render the precipitation more complete. Baryta-water is added to the fluid filtered off from the precipitate, until it is slightly alkaline; it is then evaporated to dryness on the water-bath, redissolved in water, filtered, and the filtrate treated as above

directed. Another method, which may be adopted for determining the amount of nitric acid in the nitrates, is to distil the nitrate with sulphuric acid diluted with twice its volume of water at a temperature not above 160° or 175°. The operation is conducted in a retort with the neck drawn out, and bent so that by means of an india-rubber tube it may be connected with a little receiver with three bulbs (similar to that used for collecting ammonia in the estimation of ammonia, by the method of Will and Varrentrapp), containing a known volume of a standard solution of potassa or soda. The distillation must be continued for three or four hours. It may be effected in a water-bath in a vacuum, either by means of an air-pump, or by expelling the air from the apparatus by boiling, and then closing hermetically. If the nitrate is mixed with chloride, a solution of sulphate of silver, or of moist oxide of silver, is added previous to distillation (Rose).

For estimating nitric acid in the indirect way, Reisch has proposed heating the nitrate at a barely visible red-heat, with four or six times their weight of pulverized *quartz*, which he prefers to bichromate of potassa, because the mass calcines without melting, and there is therefore no fear of portions being projected from the crucible, and because the presence of chlorides and sulphates is no inconvenience, the nitrates alone being decomposed.

Crum (Journ. für Prakt. Chem., 41, 201) estimates nitric acid by transforming it into binoxide of nitrogen. The salt dissolved in water is introduced into a graduated jar over mercury, and then sulphuric acid added to the extent of three times the volume of the water used,—after a few hours the binoxide is disengaged; the volume of the gas in the tube is measured, due regard being had to the temperature, and the height of the barometer; the binoxide is then absorbed by throwing up into the tube a solution of protosulphate of iron, and the amount of absorption being carefully noted, the quantity of nitric acid is calculated therefrom. Schlösing (Journ. für Prakt. Chem., 62, 142) also converts the nitric acid into binoxide, but instead of measuring the volume of the gas he reconverts it into nitric acid. The solution of the nitrate is boiled in a flask, till all the air is expelled; an acid solution of protochloride of iron is then drawn into the flask, and the liquid is again boiled, binoxide of nitrogen is evolved, which is collected over mercury in a balloon filled with mercury and milk of lime: the gas

is then brought, without loss, into contact with oxygen and water, so as to convert it again into nitric acid, which is estimated with normal alkali in the usual manner. This method, which may be used in the presence of organic matter, "has passed successfully," observes Fresenius (Quant. Anal., p. 309), "through an ordeal of numerous and searching experiments." It was devised by the author for estimating the amount of nitric acid in tobacco.

Valuation of Nitre.

1. *Method of Pelouze* ('Comptes Rendus,' January, 1847).—This is founded on the peroxidation of a protosalt of iron by the oxygen of the nitric acid, a solution of permanganate of potassa being employed, as in Marguerite's process (see IRON), to indicate the completion of the oxidation. The operation is as follows:—It is first accurately determined how much pure nitrate of potash is requisite to peroxidize a known weight of iron dissolved in excess of hydrochloric acid. Pelouze found that 2 grammes of pure iron (pianoforte wire) dissolved in a considerable excess of hydrochloric acid, required from 1·212 to 1·220 gramme; on an average therefore 1·216 gramme of pure nitrate of potash. He examined the nature of the gases given off in this reaction, and found them to consist of hydrochloric acid and binoxide of nitrogen. Converting these numbers into equivalents, they correspond to 6 equivalents of iron and 1 equivalent of nitrate of potash: the acid of this last salt is decomposed, therefore, into binoxide of nitrogen, which is disengaged, and into 3 equivalents of oxygen, which deprive the hydrochloric acid of 3 equivalents of hydrogen to form 3 equivalents of water and liberate 3 equivalents of chlorine, which produce with the 6 equivalents of protochloride of iron 3 equivalents of perchloride. These reactions will be better understood by putting them into an equation, thus:—

$$6FeCl + KO,NO_5 + 4HCl = \\ 4HO + KCl + NO_2 + 3(Fe_2Cl_3).$$

It will be observed, by the way, that this decomposition of nitrates by protosalts of iron in the presence of an excess of hydrochloric acid furnishes a method of preparing binoxide of nitrogen. This decomposition being established, it occurred to Pelouze that it might be made the basis of a ready and simple method of analysing the nitrates. He found that the presence of sulphates and chlorides in no way interfered with the decom-

position in whatever proportion they were present, and there only therefore remained to be found, a safe and ready method of determining, in the assay of an impure nitrate, the quantity of iron not peroxidized. Such a method has been described by Marguerite. Suppose, for instance, that having operated upon 30·88 grains of iron, and 18·77 grains of impure nitre, the permanganate of potassa indicates that 3·088 grains of iron have not been peroxidized, it may be concluded that 30·88 grains minus 3·088 grains, or 27·79 grains, have been peroxidized: now, if the nitre had been pure, the whole 30·88 grains would have been peroxidized; we, therefore, have the proportion—

As 30·88 : 18·77 : : 27·79 : 16·89;

the 18·77 grains of impure nitre consequently contain 16·89 grains of nitrate of potash, or 90 per cent.

The following example will illustrate the practical details of the method. The specimen may be supposed to be taken from a sample of the crude nitre of commerce as it is sent to the refiner.

30·88 grains of pianoforte wire are placed in a flask of the capacity of about 10 cubic inches, and on them are poured about 1500 grains of strong hydrochloric acid, the flask is closed with a cork furnished with a drawn-out tube, and the iron dissolved at a gentle heat. When the whole is dissolved, 18·52 grains of the nitre under examination are introduced, the flask is immediately closed, and the liquid boiled; it becomes of a brown colour; dense vapours of hydrochloric acid, mixed with binoxide of nitrogen, issue from the orifice of the drawn-out tube, and prevent the access of air. As soon as the liquor loses the brown colour, it becomes yellow, and gradually brightens: after boiling for 5 or 6 minutes, and when the liquid has become perfectly transparent, the flask is removed from the fire, the liquid which it contains, and the wash water are poured into a flask capable of holding about 60 cubic inches, which is then entirely filled with ordinary water: upon this a solution of permanganate of potash of known strength is gradually added from a graduated burette. The operation is then finished, and there remains only to calculate the result.

Let us suppose that the solution of permanganate was of such a strength that 25 divisions of the burette were required to peroxidize 7·72 grains of iron, or 50 divisions for 15·44 grains of that metal; and let us further suppose that to complete the preceding experiment 10 divisions of the same solution were

required; now, if 50 divisions of this permanganate suffice to peroxidize 20 of iron, how much ought 10 divisions to peroxidize?

As 50 : 15·44 :: 10 : 3·088.

3·088 therefore are subtracted from 30·88 grains of iron, and it may be concluded that the remaining 27·888 have been peroxidized by 18·52 grains of crude nitre: but it is known that 30·88 grains of iron represent 18·77 grains of pure nitrate of potash, the quantity of that salt therefore corresponding to 27·888 grains of iron is found by the following proportion:—

As 30·88 : 18·77 : : 27·888 : 16·95.

In the 18·52 grains of saltpetre submitted to analysis there were therefore 16·95 grains of pure nitre = 91·4 per cent. In performing the experiment the operator must be careful in guarding against access of air: otherwise this would be apt to act upon the binoxide of nitrogen, and render it capable of peroxidizing a further quantity of iron, so that the amount of nitre would be exaggerated. However, the peroxidation of iron, when the metal is dissolved in a strongly acid liquid, is very slow, as Marguerite has shown, and in the manner of conducting the process, as described above, the inconvenience is avoided, for as soon as the iron has disappeared in the acid the flask is filled with hydrogen and hydrochloric acid gases: the nitrate which is introduced carries with it but a mere trace of air, and the liquid kept boiling disengages, by the drawn-out tube, acid and aqueous vapours, the issuing forth of which being always visible and readily maintained, does not allow the admission of any air.

Pelouze states that he has confirmed the accuracy of his method by the analysis of several other nitrates, such as those of soda, ammonia, lead, etc., and he observes further that it will enable us to determine the amount of water in certain nitrates, the composition of which is at present doubtful.

This method has been subjected to an elaborate critical examination by Abel and Bloxam (Quart. Jour. Chem. Soc., vol. ix. 97). They have arrived at the conclusion, that although the reaction upon which it is founded is perfectly correct, and that therefore it frequently happens that the most accurate results are furnished by it, nevertheless, these results are liable to contain disturbing causes which are so far beyond the control of the operator as to deprive the method of that certainty so essential to any process in use for commercial analysis. These

disturbing causes are:—1. The action of air upon the nitric oxide gas by which nitric acid is re-generated. 2. The incomplete expulsion of the nitric oxide from the fluid, in consequence of which it reduces a larger quantity of permanganate of potassa than corresponds with the amount of protoxide of iron contained in it; this however is only to be feared in dilute solutions. 3. The evolution of nitric acid *before* it has acted upon the protochloride of iron, especially when the fluid boils very rapidly after the addition of the nitrate, and when the excess of protochloride of iron is proportionally small. All these sources of error may, according to Fresenius (Liebig's 'Annalen,' May, 1858, p. 217), be avoided, and perfectly satisfactory results obtained, by the following method of operating. Into the belly of a tubulated long-necked retort, capable of containing about 200 cubic centimètres, so fixed that the neck is directed a little obliquely upwards, is put about 1·5 gramme of fine pianoforte wire, accurately weighed, and from 20 to 40 cubic centimètres of *pure* fuming hydrochloric acid are added. Hydrogen gas washed in a solution of potash, is now passed in through the tubulure by means of a glass tube reaching about 2 centimètres into the retort, and the neck of the retort is united to a U-shaped tube containg a little water. The belly of the retort is placed on the water-bath, and gently heated, till the iron is completely dissolved. It is then allowed to cool in the current of hydrogen, which is afterwards strengthened, and the nitrate weighed in a small tube is thrown in with the tube, through the neck of the retort. The quantity of the nitrate should be calculated, so that it may only contain about 0·200 gramme of nitric acid. After the union of the neck of the retort with the U tube, the contents of the retort are heated on the water-bath for about a quarter of an hour, the water-bath is then removed, and heat is applied by a lamp so as to produce strong ebullition, until the solution, which has a dark colour from the absorbed nitric oxide gas, has acquired the colour of perchloride of iron, after reaching this point, the boiling is continued for a few minutes. Every time the fluid is agitated, care must be taken that dry salt is never deposited on the walls of the retort. Before the boiling is stopped, the current of hydrogen gas is strengthened in order to prevent the entrance of air through the U tube when the lamp is removed. The retort is allowed to cool in the current of hydrogen, the contents are much diluted with water, and finally the iron still existing

as *protoxide*, is determined with solution of permanganate of potassa.

This method may, according to the author, be employed with the greatest confidence when no organic matters are present.

Instead of estimating the amount of protoxide of iron on which the nitric acid has not acted, by permanganate of potassa, Braun (Journ. für Prakt. Chem., lxxxi. 421) determines the amount of peroxide formed, by means of iodide of potassium and hyposulphite of soda. The perchloride of iron decomposes the iodide of potassium, and sets the iodine at liberty, even in the cold, but more completely when the reaction is assisted by a gentle heat. The free iodine is estimated by a normal solution of the hyposulphite, after having added a small quantity of starch paste. The normal solution of hyposulphite of soda is prepared either by dissolving a known weight of the salt in a similarly known weight of water, or by standardizing with a solution of hyposulphite of unknown strength, the iodine set free by perchloride of iron prepared from a known weight of metallic iron.

II. *Gay-Lussac's method, modified by Abel and Bloxam.*—The nitrate is converted into carbonate by fusion with charcoal, and the amount of alkaline carbonate is determined by a standard solution of sulphuric acid. In order to moderate the evolution of nitrogen gas, a certain quantity of pure common salt is added to the mixture. The proportions usually employed, are 1 part of lamp-black, 4 of nitre, and 24 of salt, to 20 of nitre. The nitre and charcoal are first mixed in a platinum crucible with a glass rod, the chloride of sodium is then added, and an intimate mixture of the whole is made. The crucible is covered and heated, cautiously at first, to prevent too violent deflagration, and afterwards for a few minutes at a red temperature; when cold, the contents of the crucible are washed into a flask, treated with hot water, the residual carbon filtered off, and the alkalinity of the solution then determined by a normal solution of sulphuric acid.

Abel and Bloxam, who have thoroughly investigated this method, likewise (Quart. Journ. Chem. Soc., vol. ix. p. 110, and vol. x. p. 107) employ an acid so far diluted that a little less than 1000 grain-measures are required to neutralize the amount of carbonate of potassa, corresponding to 20 grains of nitre. An acid of this description contains from 8·0 to 8·5 grains of anhydrous acid in 1000 grain-measures. The strength

of the acid having been approximately ascertained by the neutralization of a known weight of carbonate of soda, is finally determined with the greatest possible accuracy by precipitation as sulphate of baryta. In performing the alkalimetrical assay a sufficient quantity of aqueous solution of litmus is added to impart a deep blue colour to the liquid; the standard acid is then added until it acquires a wine-red tint from the dissolved carbonic acid; the liquid is then boiled, and the acid very carefully added, drop by drop, until the peculiar *onion-skin red* colour imparted by the stronger acids to litmus, is obtained. The accurate appreciation of the colour is much facilitated by using as a standard of comparison, a similar quantity of coloured water to which a few drops of sulphuric acid have been added.

A great number of experiments made by Abel and Bloxam disclosed a considerable uncertainty in the above method; this they traced to the following facts:—1. That a considerable quantity of nitre may escape decomposition at a high temperature, even when intimately mixed with an excess of finely divided carbon, and although vivid deflagration of another portion of the nitre had taken place in its immediate neighbourhood. 2. That in the deflagration of a mixture of nitre, salt, and charcoal, *binoxide of nitrogen* is evolved in large quantity. 3. That in the deflagration, *cyanide of potassium* is formed, and that, even where much care had been taken to remove moisture from the materials, a notable quantity of *ammonia* is evolved. 4. That the oxidation of cyanide of potassium by exposure to the air at a high temperature is not prevented by the presence of carbon in a finely divided state, or even by covering it with a layer of carbon. By substituting pure, ignited, and finely divided graphite for charcoal, in the conversion of the nitre into carbonate of potassa, and by the subsequent treatment of the fused mass with chlorate of potassa in order to oxidize the cyanate of potassa formed by the oxidation of the cyanide of potassium, and to obviate the errors which may arise from the reduction of any sulphates which may be present, Abel and Bloxam succeeded in obtaining very accurate results. The proportions they recommend are 20 grains of nitre, 5 grains of ignited graphite, and 80 grains of pure common salt. The crucible, covered with a jacket, should be loosely covered, and moderately heated for two or three minutes over the gauze gas-burner; it should then be allowed to cool to such an extent

that chlorate of potassa shall not fuse when sprinkled upon the mass. About 25 grains of the chlorate are added, so as to form a layer upon the surface. A very gentle heat is first applied, until most of the chlorate has been decomposed, when the temperature is raised to bright redness, and maintained in that state for two or three minutes; when cool the mass is to be carefully shaken out of the crucible into a funnel, and the crucible and cover washed with boiling water. The mass is dissolved by a stream of hot water from a washing-bottle, and the solution allowed to run into the flask in which the determination is to be made; the liquid is coloured with litmus, and neutralized with the standard acid.

Estimation of Nitric Acid by conversion into Ammonia (Schulz, Chem. Centralblatt, No. 58; and Vernon Harcourt, Journ. Chem. Soc., vol. xv. p. 381).—When a moderately concentrated solution of potassa is poured upon a mixture of iron and zinc, hydrogen gas is freely disengaged, even without the application of heat; the action is electrolytic; the zinc is oxidized, and the hydrogen formed upon the surface of the iron. If a nitrate be added to the mixture evolving hydrogen, ammonia is immediately produced. This reaction furnishes a good qualitative test for nitric acid. The fluid to be examined is reduced to a small bulk, and poured into a test-tube containing a mixture of granulated zinc and clean iron filings; a small quantity of strong solution of potassa is then added; the mixture is heated, and the gases evolved are led into a small quantity of dilute hydrochloric acid. The acid solution is supersaturated with potassa, and tested with a drop of potassio-iodide of mercury (p. 64). To apply this reaction to the quantitative determination of nitric acid in a nitrate, Harcourt proceeds as follows:—A flask, having a capacity of about 12 cubic inches, is connected by a bent tube drawn out and recurved at its extremity, with a smaller flask or bulb, and the two are so arranged that they both rest at a considerable angle of inclination, upon a sand-bath. The smaller flask, into which a little water is poured, is connected with a condenser which leads into a tubulated receiver containing normal sulphuric acid coloured with litmus; the end of the distilling-tube reaches to about the middle of the receiver, through the tubulure of which is inserted a tube with two or more bulbs, containing also coloured normal acid. In the upper part of the condensing-tube is a small tubulure; during the process of distillation, this is closed

by an india-rubber plug, which may be removed after the operation, is over for the purpose of sending a stream of water down the tube to remove all traces of ammonia from its sides. Into the larger, or distilling flask, are introduced 700 or 750 grains of granulated zinc, with about half that quantity of clean iron filings, which have been recently ignited in a covered crucible, then the weighed nitrate with water sufficient to dissolve it, and lastly, a considerable excess of strong solution of caustic potassa; the flask is immediately connected with the condensing apparatus and heat applied; when the distillation has actually commenced the water in the second flask is made to boil gently: by this arrangement the fluid is twice distilled, and any traces of potassa which may have passed over from the distilling-flask are sure to be retained. In his experiments with nitre, Harcourt has generally taken 0·5 grain of that substance, 20 cub. cent. of water, and the same volume of solution of potassa, sp. gr. 1·3; with these quantities the distillation occupies about an hour and a half; it is completed when the hydrogen is pretty freely liberated, as the potassa becomes concentrated; the lamp is then removed, and the whole allowed to cool; the distilling-tube is rinsed into the receiver, and the determination is completed by adding standard alkali from a burette to the fluid in the receiver till a change of colour appears; with alkaline nitrates this method gives very exact results; with the nitrates of the heavy metals the results do not appear to be quite so satisfactory.

Pugh's method (Quart. Journ. Chem. Soc., vol.xii. p. 35).—This process is based on the fact that when a nitrate is digested under pressure at a temperature of about 320° F., with an excess of protochloride of tin, and hydrochloric acid, the following reaction occurs:—

$$NO_5+8(SnCl+HCl)=NH_3+8(SnCl_2)+5HO.$$

1 equivalent of nitric acid therefore, under the above conditions, converts 8 equivalents of tin from proto- to perchloride; consequently if an unknown quantity of nitric acid be digested with sufficient excess of solution of protochloride of tin of known strength, and the quantity changed into perchloride be afterwards found by a suitable method of titration, the proportion of nitric acid will be found,—supposing in all cases that no other substance is present capable of effecting the same change in the tin solution. For the purpose of estimating the amount of tin oxidized, Pugh adopts the method proposed by

Streng (Pogg. Ann. xcii. 57), which consists in ascertaining how much of a solution of bichromate of potassa of known strength, is necessary to convert a given amount of protochloride of tin in hydrochloric acid into perchloride, the point of complete chloridation being known by the deep blue colour produced by the liberation of iodine from iodide of potassium, in the presence of starch, by the first drop of bichromate of potassa solution above that necessary to raise the protochloride to perchloride. According to Sutton, however ('Volumetric Analysis,' p. 60), this method is not satisfactory, owing to the variable amount of oxidation which the tin solution undergoes when different quantities of water or acid are present during the titration; he therefore adopts the following method proposed by Lessen:—Metallic tin or its protosalt is dissolved in hydrochloric acid, if not already in solution, a tolerable quantity of the double tartrate of soda and potassa added, together with bicarbonate of soda in excess. If enough tartrate is present the solution will be clear; starch liquor is then added, and the mixture titrated with a decinormal solution of iodine, till the blue colour is permanent. For details respecting this elegant volumetric method we must refer to Pugh's memoir, or to Sutton's very useful work, referred to above.

204. Chloric Acid.

When this acid exists in a free state in aqueous solution, it is most simply estimated, according to Fresenius, by converting it into hydrochloric acid by means of sulphurous acid, in the following manner:—The solution is mixed with a considerable excess of an aqueous solution of sulphurous acid, and well agitated; the flask is then stopped, and its contents digested for some time. The excess of sulphurous acid is then removed by bichromate of potassa, and the liquid, being acidified with nitric acid, is precipitated with nitrate of silver, and the amount of chloric acid originally present calculated from the quantity of chloride of silver obtained.

Chlorates are analysed either by measuring the volume of oxygen gas which they evolve by their decomposition, or by exposing a known weight to ignition and calculating the amount of chloric acid from the loss of weight thereby experienced; should the salt under examination contain water of crystallization, it must be ignited in a retort of hard glass, to

which there is attached a weighed tube containing chloride of calcium.

When a *chloride* and a *chlorate* are contained in the same solution, and are each to be estimated, the amount of chlorine in the chloride is first determined in a weighed quantity of the solution, by precipitating it as chloride of silver, another weighed portion of the solution is evaporated to dryness and ignited, by which the chlorate present is converted into chloride, it is then redissolved in water, and precipitated by nitrate of silver; from the amount obtained we have merely to deduct that yielded by the first experiment to obtain the requisite data for calculating the quantity of chloric acid.

CHAPTER IX.

ON THE ELEMENTARY ANALYSIS OF ORGANIC BODIES.

205. Numerous and diversified as are the forms and properties of vegetable and animal substances, and complex as is, in general, their composition, they are nevertheless made up of a very few of the so-called elements of the material world. A vast number of organic substances consist but of three of these elements, viz. *carbon*, *hydrogen*, and *oxygen*,, and very many contain only two, *carbon* and *hydrogen*. There is, again, a very large class of organic bodies into the composition of which *nitrogen* enters in conjunction with *carbon*, *hydrogen*, and *oxygen*, and there are others to which, together with these four principles, *sulphur* and *phosphorus*, *iron*, *manganese*, and a few other elements appear to be essential. Thus, of the sixty-three substances at present recognized by chemists as elementary, not more than ten or a dozen are found in the organic world. It is true that organic compounds *may* contain other bodies; but such are of artificial production, and do not therefore militate against the fact we have just stated, viz. that by far the greater number of that almost bewildering variety of substances which we meet with as the products of animal and vegetable life, and of their reactions on each other, are constituted of three or four only of the elementary bodies, and that about a dozen of them are the most that are ever found to enter into their composition.

The older chemists, being unacquainted with any methods of resolving organic substances into their ultimate constituents, or of re-arranging their elements into such forms of combination as might enable them to pronounce upon their constitution, were obliged to satisfy themselves with the examination of the results of their destructive distillation; they thus resolved them into a series of products which, being liable to infinite variation dependent upon the manner in which the distillation

was effected, and the degree of heat employed, could, it is obvious, throw but little light on the composition or properties of the substance under examination. A vast number of analyses were, however, made in this way by the earlier pneumatic chemists, of whom Hales and the celebrated Priestley studied attentively the gaseous products of the operation.

The first chemists who attempted to combat the difficulties which surrounded the original attempts to gain an insight into the composition of organic substances, by the examination of the results of their combustion in oxygen, were Gay-Lussac and Thenard. Their method was to mix a certain weight of the substance to be analysed into one or more pellets with chlorate of potassa, and to drop them, by a suitable contrivance, into an ignited glass tube, receiving the product of the combustion into a jar filled with mercury and inverted in a mercurio-pneumatic apparatus. It was soon found, however, that a perfect combustion of the substance could not be effected with chlorate of potassa, in consequence of the sudden manner in which this salt liberates its oxygen when exposed to heat. Gay-Lussac therefore suggested the employment of oxide of copper, a substance which does not decompose when ignited alone, but which readily yields its oxygen when heated strongly with an organic substance. The idea of using this oxide was a very happy one, and there can be no doubt that we owe to its application, in a great measure, that vast addition which has of late years been made to our knowledge in this department of chemistry.

Dr. Prout employed an entirely different method; it was complicated, though exceedingly accurate, as is evident from the fact that the analyses performed by its distinguished inventor, are still regarded as models of scientific research, and from the circumstance that Dumas was induced to recur to it notwithstanding its complexity. Dr. Prout's object was to burn the substance effectually in oxygen gas; in which case, supposing it to contain three elements,—hydrogen, carbon, and oxygen,—one of three things must happen:—1st, the original bulk of the oxygen must remain the same, in which case the hydrogen and oxygen in the substance exist in it in the same proportion in which they exist in water; or 2nd, the original bulk of the oxygen is increased, in which case that element must exist in the compound in a *greater* proportion than it exists in water; or 3rd, the original bulk of the oxygen is *diminished*, in which case the *hydrogen* must predominate. In the first case, the compo-

sition of a substance may be known by determining the quantity of carbonic acid gas yielded by a known quantity of it; while in the other two, the same can be readily ascertained from the same data, by noting the excess or diminution of the original bulk of oxygen. For full details respecting the manner of conducting the whole operation, the student is referred to Dr. Prout's original paper in the Philosophical Transactions for 1827, or to an abstract of the same in Brande's 'Manual of Chemistry,' where he will also find woodcut illustrations of the different parts of the apparatus. We must content ourselves here with a general statement of the advantages of this method of analysing organic compounds, as summed up by the inventor. In the first and chief place, there is nothing to be apprehended from moisture. Whether the substance to be analysed be naturally a hydrate, or in whatever state it may be with respect to water, the results will not be affected; and the great problem whether the hydrogen and oxygen exist in the substance in the proportions in which they form water, or whether the hydrogen or the oxygen predominates, will be equally satisfactorily solved, and that (within certain limits) independently of the weight of the substance operated on. When, however, it is the object to ascertain the quantity of carbonic acid gas and water yielded by a substance, it is of course necessary to operate on a known weight; but this being once determined, there is no fear, as in the then common methods, of exposing the substance to the atmosphere as long as may be necessary. The hygrometric properties of the oxide of copper, as well as its property of condensing air, are also completely neutralized, for the whole, at the end of the experiment, being left precisely in the same state as it was at the commencement, the same condensation of course must take place, and any little differences that may exist, are rendered quite unimportant from the bulk of oxygen gas operated on, which of course, in all cases, should be considerably greater than that of the carbonic acid gas formed. Another advantage of this method is, that *perfect combustion* is ensured by it. There is, also, no trouble of collecting and estimating the quantity of water, a part of the common process attended with much trouble, and liable to innumerable accidental errors; here, on the contrary, the results are obtained in an obvious and permanent form, and, from the ease with which they are thus verified, comparatively very little subject to error.

We shall now proceed to describe, somewhat in detail, the more

modern methods of analysing organic substances, for the perfection of which the scientific world is mainly indebted to Baron Liebig. This method combines with great exactness such simplicity of execution, that it is frequently resorted to as the easiest method of testing the purity of a substance; and it is generally admitted that to its invention must be ascribed the rapid progress of organic chemistry within the last few years. The process consists in burning the organic substance together with oxide of copper or chromate of lead, by which its carbon is converted into carbonic acid and its hydrogen into water, both of which are collected and weighed; if the body contain nitrogen, it is either collected in a gaseous state, or is determined by other methods, and the oxygen is calculated by deducting from the original weight of the substance analysed, the combined weights of the carbon, hydrogen, and nitrogen formed.

206. *Preliminary testing of the Organic Substance.*—Before commencing the ultimate analysis of an organic compound, the operator must assure himself of its purity. The presence or absence of inorganic non-volatile matter is easily ascertained by heating the substance on platinum foil over a spirit lamp, and, if necessary, urging the flame with the blowpipe; if it does not wholly disappear, the residue must be minutely examined; and if it has been determined to proceed with the ultimate analysis of the compound, notwithstanding the presence of inorganic matter, the amount of the latter must be accurately ascertained. We will suppose, however, that the substance has been proved to be free from inorganic non-volatile matter; it has next to be tested for *nitrogen*, *sulphur*, and *phosphorus*.

a. *Testing for Nitrogen.*—If the quantity of this element be large it is easily detected by simply burning the body, which emits during ignition a smell of singed hair. In smaller quantities, it may be detected by mixing the substance with soda-lime, and heating it in a test-tube; the water of the hydrate is thereby decomposed, its oxygen passing to the carbon and hydrogen of the organic substance, and its hydrogen to the nitrogen (if it contain any), giving rise to the formation of ammonia, which may be detected at the orifice of the tube by holding near it a feather, moistened with strong acetic acid. The following beautiful and delicate test for minute quantities of nitrogen in organic substances, was recommended by Lassaigne (Bibliothèque Univ., April, 1843). It is based on the facility with which cyanide of potassium is formed when an organic sub-

stance, containing even very little nitrogen, is calcined at a red-heat and protected from the atmosphere, together with an excess of potassium. A small piece of this metal is placed at the bottom of a tube, and the matter to be tested is then added. The end of the tube is heated to a dark red in the flame of a lamp, then left to cool, and the potassa salt, formed by the calcination, dissolved with four or five drops of distilled water. The decanted liquor is tested with a drop of solution of ferroso-ferric oxide (magnetic oxide of iron); a dirty greenish precipitate is immediately formed, which being brought into contact with a drop of hydrochloric acid, becomes a dark blue, if the matter under examination contain a trace of nitrogen. In the contrary case, the precipitate of the hydrated oxide of iron is entirely redissolved, without any blue colouring. Lassaigne found that neither potassa nor its carbonate could be substituted for potassium in this process, neither is it applicable when the organic substance is accidentally mixed with a nitrate, or with an ammoniacal salt. Of these two methods of testing for nitrogen, the latter is in its indications the least liable to misconstruction. If the organic compound contain nitrogen in chemical combination with oxygen, the presence of that element is readily detected by heating the substance in a tube and holding over the mouth a piece of paper moistened with solution of starch, to which a drop of iodide of potassium has been added, a blue colour is imparted to the paper if nitrous or nitric acids be present.

b. *Testing for and estimation of Sulphur.*—A variety of methods have been proposed for detecting and estimating the amount of this element in organic substances. The following are the most reliable:—

I. *Rüling's process* (Chem. Gaz., vol. iv. p. 362).—The finely pulverized substance is fused in a spacious silver dish, with about twelve times its weight of caustic potassa, perfectly free from sulphuric acid; it is then mixed with pure nitre, in weight equal to about half the potassa employed, and heated till the fused mass appears perfectly white. The whole is then supersaturated with hydrochloric acid, and a salt of baryta added: the formation of a white precipitate indicates sulphur. It consists of sulphate of baryta, and is collected, washed, dried, and ignited. It weight furnishes the datum for calculating the amount of sulphur originally present in the substance.

II. *Kemp's process* (Chem. Gaz., vol. iv. p. 371). — Fine

quartz sand, which has been carefully tested for sulphuric acid, is mixed with chlorate of potassa, in the proportion of two-thirds of the former to one-third of the latter. The substance to be examined is intimately mixed with the above, introduced into a large platinum crucible, and exposed to a high temperature over a spirit-lamp. The process is completed in a few seconds. The contents of the crucible are treated with boiling distilled water, the insoluble portion separated by filtration, and washed till no traces of sulphuric acid remain: the sulphates and phosphates, if any exist, may by this plan be estimated simultaneously by means of a salt of baryta. The object of the sand is to prevent the too rapid oxidation of the organic body, and the risk of a portion being thrown out of the crucible.

III. *Weidenbusch's process* (Liebig's 'Annalen,' March, 1847).—The substance is mixed with an excess of nitrate of baryta, and stirred in a beaker glass, with the most concentrated fuming nitric acid, to a thin paste; the beaker is covered and exposed to the temperature of the sand-bath, replacing the evaporated nitric acid until the organic substance is entirely destroyed, which is perceptible from the circumstance that on evaporating the nitric acid still present, the mass begins to thicken, but no longer ascends in large bubbles in the glass, and dries quietly without frothing. The decomposed mass is now carefully washed into a platinum dish, dried at 212°, and then heated gradually, until the saline mass is perfectly liquid. If the organic substance had not been completely destroyed by the nitric acid, it frequently happens that the mass takes fire, and a portion is projected from the slight deflagration. This must be avoided, as it occasions a loss of substance; but, even though this were not the case, a smaller quantity of sulphate of baryta would probably be obtained, since it appears that the sulphur still contained in organic combination is not oxidized so readily by the deflagration of the mass, as by the slow action of the nitric acid. The fused mass is carefully removed from the platinum dish, treated with dilute acetic acid, and heat applied as long as any evolution of gas is perceptible. The carbonate of baryta is decomposed, and the residue (if any) consists of pure sulphate, which is collected on a filter, washed, dried, heated to redness, again digested with acetic acid after ignition, and again heated to redness. After the second ignition it is perfectly pure, and the amount of sulphur may be calculated from it.

IV. *Heintz's process* (Poggendorff's 'Annalen,' lxxii. p. 145).—The sulphur is converted into sulphuric acid by burning the organic substance with oxygen and oxide of copper. For this purpose an ordinary combustion-tube, open at both ends, is half filled with copper turnings, and a little vessel containing the dry and pulverized substance placed in the tube, which is then connected with a bulb apparatus, filled with solution of potassa, perfectly free from sulphuric acid, and the combustion made in a current of oxygen. The contents of the bulb apparatus are now decanted into a spacious flask, containing a warm solution of chlorate of potassa in dilute nitric acid, and closed with a glass stopper. The sulphurous acid absorbed by the potassa, and which had formed from the decomposition of a portion of the sulphate of copper, is by this means perfectly oxidized. The mixture of oxide, sulphate, and metallic copper is treated in a beaker with the above mixture, and entirely dissolved at a gentle heat; the sulphuric acid is precipitated by chloride of barium, and estimated as usual. As, along with the sulphurous acid, sulphuric acid always passes over into the bulb apparatus, it is advisable, in order to avoid all loss of sulphuric acid, which might arise from condensation of the latter on the cork of the combustion tube, to employ a tube which is drawn out at one extremity at a very obtuse angle into a fine tube, which fits into the stronger arm of a bulb apparatus made for the purpose, and then connected with caoutchouc. The author examined *taurine* by this process, and found in three experiments, in the first, 25·68; in the second, 25·66; and in the third, 25·49 per cent. of sulphur. Redtenbacher's formula, $C_4H_7NO_6S_2$, requires 25·60 per cent. The combustion must not be carried on too quickly, otherwise a slight loss might readily occur from vapour passing through the solution of potassa without being absorbed thereby. In illustration of the importance of carefully examining organic substances for sulphur, and of the great mistakes which may be committed from neglecting to do so, it may be mentioned that the substance above alluded to, viz. *taurine*, which contains nearly 26 per cent. of sulphur, had originally assigned to it the formula $C_4H_7NO_{16}$ and was supposed to be altogether free from that element.

V. *By Acetate of Lead.*—A very convenient method of detecting minute quantities of sulphur in organic substances, which does not, however, enable us quantitatively to estimate

it, is to boil the compound nearly to dryness with a concentrated solution of caustic potassa. The residue is dissolved in water, and introduced into a flask provided with a tube funnel; a strip of paper which has been thoroughly moistened with acetate of lead, and subsequently touched with a few drops of carbonate of ammonia, is suspended inside the flask between the cork and the neck; on pouring a little dilute hydrochloric acid slowly through the tube-funnel, sulphuretted hydrogen gas will be evolved, should sulphur be present, and the lead-paper will turn brown.

c. *Testing for, and estimation of Phosphorus.*—The substance may be oxidized by the process of either Rüling or Kemp, or with fuming nitric acid, or with a mixture of nitric acid and chlorate of potassa, and the solutions obtained may be examined for phosphoric acid by one of the methods described in the section on "PHOSPHORIC ACID."

(1.) *Analysis of non-volatile Solids, not containing Nitrogen.*—The first important point is to dry the substance thoroughly. This is done either in the water or air-bath, or *in vacuo* over sulphuric acid, or by any other of the methods described in the first chapter of this treatise, the means employed depending on the physical and chemical characters of the substance under examination. With the view of illustrating the details of the whole operation, we will take, as the simplest case that can be brought before the student, the analysis of the crystallizable sugar of manna, namely, *mannite*, giving the results as they occurred in an actual analysis.

The crystalline sugar, having been finely pulverized, is dried in a watch-glass in the water-bath until two weighings, made at the interval of half an hour from each other, furnish a constant result. The fine powder is now introduced into a small stoppered bottle, the exact size and shape of Fig. 85. The weight of the bottle (which is kept in the water-bath along with the substance, to ensure its being thoroughly dry) is, when empty 76·66 grains, and, when filled with the mannite, 84·76 grains.

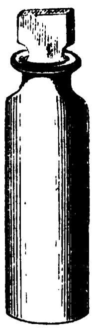


Fig. 85.

A Hessian crucible, of the capacity of about four ounces, is nearly filled with oxide of copper, carefully prepared in the following manner:—Some shreds of pure copper (clippings from elec-

trotypes) are dissolved in pure nitric acid; the solution is evaporated to dryness in a porcelain basin, and the residual basic salt heated to moderate redness in a Hessian crucible, until fumes of nitrous vapour cease to be evolved. It is constantly stirred during the ignition with a copper rod, to promote the escape of the gas. The last traces of nitric acid adhere somewhat obstinately to the oxide of copper; the process should not, therefore, be hurried, but it is better to keep up a moderate heat for a considerable time than to attempt to quicken the operation by urging the fire, as in this case the lower portions of the oxide are apt to fuse, and, on cooling, the mass becomes so hard that it is difficult to remove it from the crucible, and subsequently, to reduce it to powder. Before considering the process to be finished, a portion of the oxide should be tested; with which view a small quantity is introduced into a tube of combustion glass and strongly heated, the aperture of the tube being closed with the finger. On removing the latter the smell will generally indicate the existence of nitrous vapours, and the tube itself should be carefully examined for the appearance of ruddy fumes. The decomposition being complete, the oxide is allowed to cool, then transferred to a mortar, in which it is reduced to a tolerably fine powder, after which it is fit for use, and may be preserved in a wide-mouth stoppered bottle. The same oxide may be employed for several experiments: by merely pouring a little acid on it, the metal is oxidized afresh, and the oxide is restored to its former purity by calcination. The Hessian crucible above alluded to is nearly filled with oxide of copper thus prepared:—its cover is put on, and it is placed among the coals of a coal or charcoal fire, taking the greatest care that no organic matter from the fire comes accidentally into contact with it. It is heated to low redness: meanwhile, the other materials required for the analysis are being prepared.

(a.) *The Combustion Tube.*—This is drawn out from a tube of hard German glass, with the aid of a blowpipe lamp (Fig. 13, p. 20). A tube free from flaws, and which has been previously tested as to its capability of bearing the requisite heat without blowing out, is selected, from thirty inches to three feet long; it is heated, first gradually, and then with the full power of the lamp, in the middle, until it becomes sufficiently soft to rend asunder; the two ends are then drawn from each other, and by a dexterous turn of the wrist two tubes are prepared, shaped as

shown in Fig. 86, each from fifteen to eighteen inches long. The fine points of the tubes are then sealed, and the open ends are fused at the edges, so as to enable them to bear the pressure of the cork without splitting. The tube, which is selected

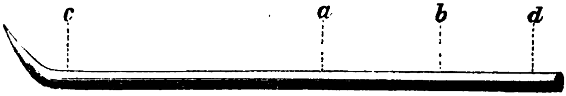


Fig. 86.

for the combustion, is thoroughly cleaned and dried; for this purpose a piece of clean filtering-paper is twisted round the end of a long stout copper wire, and with this the tube is well wiped out; it may perhaps be necessary to wash it out with distilled water. In this case, the greatest care must be taken to dry it thoroughly afterwards, which may be done either by folding loosely over the mouth a piece of filtering-paper and burying it in the sand of the sand-bath, or by heating it from end to end over a spirit-lamp, drawing a current of air through it the whole time by putting a long tube, open at both ends, to the bottom, and sucking with the mouth. If the tube has been washed out with water, a small drop of the liquid will often obstinately remain at the very point of the sealed end, which is expelled with a sort of explosion on putting the point into the flame of a spirit-lamp. The tube being thus cleaned and dried, is kept corked till about to be used, in order to prevent the entrance of any impurity.

(b.) *The Chloride of Calcium Tube.*—This is shown in Fig. 87. The chloride of calcium is prepared by dissolving chalk in hydrochloric acid, filtering the solution, and evaporating it to dryness; the dry mass is then fused in a Hessian crucible: it must

Fig. 87.

be kept in a well-stopped bottle. In filling the tube, a little cotton wool is first introduced at the large end, which is then closed with the finger; vigorous suction is now applied at the small end (seen in the figure with its cork attached), the finger is then suddenly removed, and the cotton is forced up to the end of the bulb, where it acts as a plug in preventing any of

the small fragments of the chloride from getting into, and choking up, the narrow neck of the tube. The bulb is next filled with coarse pieces of chloride of calcium, and the remainder of the tube, to within half an inch of the end, is then filled up with finer fragments; a second plug of cotton-wool is introduced, and finally the tube is closed with a good sound cork, well secured with sealing-wax, nicely smoothed round the edges; through the centre of this cork there proceeds a piece of stout quill tube about three inches long, through which connection is established between the chloride of calcium tube and the potassa apparatus. A small hook is seen in the figure attached to the tube. This is made of platinum wire, and is intended to offer a facility for hanging the apparatus to the scale of the balance, in which it is accurately weighed.

(c.) *The Potassa-apparatus.*—The construction of this apparatus (the invention of which by Liebig may be considered as one of the leading causes of the rapid progress of organic chemistry within the last few years, from the remarkable manner in which it has facilitated the analysis of organic bodies) will be understood by reference to Fig. 88. It consists of a tube on which five bulbs are blown, three at the bottom, the middle of which is the largest, and one on each of the sides; the three bottom bulbs communicate with each other by pretty wide openings, but each outer bulb is separated from the other by about two inches of tube; one of the side bulbs, *b*, must be larger than either of the others. The object of this arrangement is to expose a large surface of caustic potassa ley to the gases evolved during the combustion of the organic substance, so as to ensure the complete absorption of the carbonic acid. The method of filling the bulbs with the alkaline ley is shown in Fig. 89. A porcelain basin is filled with a solution of caustic potassa, specific gravity about 1·27. This is prepared in the usual manner, or more conveniently by the following receipt, given by Dr. Gregory ('Instructions for the Chemical Analysis of Organic Bodies,' by Justus Liebig, translated by Gregory):—Two parts of the carbonate of potassa are dissolved in twenty or twenty-four of boiling water. One part of quicklime is slaked by being covered with hot water in any convenient vessel. In this way the whole of the lime

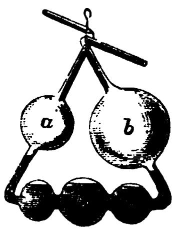


Fig. 88.

is converted into a uniform cream, without the formation of any hard sandy particles which occur in the ordinary method of slaking. The cream of lime is added in small portions to the boiling solution of carbonate of potassa, which is boiled a few minutes after each addition, water being occasionally added to supply the loss by evaporation. When the whole of the lime has been added, the mixture is boiled for a short time longer, and is then allowed to cool, the cover of the vessel being carefully closed. After twelve hours the whole of the ley may be decanted perfectly clear and quite caustic, if the vessel has been nearly full. The carbonate of lime is sandy, and occupies a very small bulk. The clear liquid is now to be boiled down rapidly in a clean iron vessel, till small crystals begin to separate. It is then allowed to cool in a stoppered bottle of green glass, when it deposits the whole of the sulphate of potassa originally present in the carbonate, that salt being entirely insoluble in a strong solution of caustic potassa. The specific gravity of this ley is from 1·25 to 1·27; it is nearly pure, containing no foreign matter except a little chloride of potassium, and is perfectly adapted for organic analysis.

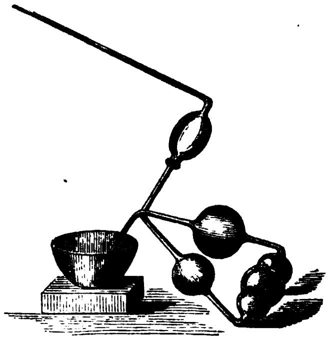


Fig. 89.

The basin being filled with the ley, the end of the tube communicating with the largest of the side bulbs, is dipped into the liquor, and to the extremity of the tube, communicating with the smaller bulb, a suction tube is attached by means of a perforated cork: suction is now applied with the lips, and the ley is thus drawn into the apparatus to the extent shown in Fig. 88. The bulbs are then moved from their inclined position, the suction tube taken off, and the interior of the tube which had been immersed in the alkaline liquor is wiped dry with a twisted slip of filtering-paper; and finally, the whole apparatus is wiped thoroughly dry with a clean cloth. It is now accurately weighed, being suspended from the pan of the balance in the manner shown in Fig. 42, p. 218.

(d.) *The Combustion Furnace.*—This is shown in Fig. 90. It is made of sheet iron, from 20 to 24 inches long, and 4 inches high. The bottom is 3 inches wide, and is furnished with a series of small slips or apertures, which serve as a grate. The side walls are slightly inclined outwards, and are, at the top, about 5 inches apart. To support the combustion-tube, a series of straight and upright pieces of strong sheet-iron are riveted to the bottom of the furnace, between the apertures; they are of exactly equal heights, and their upper edges are slightly curved, so as to coincide exactly with the aperture at the end

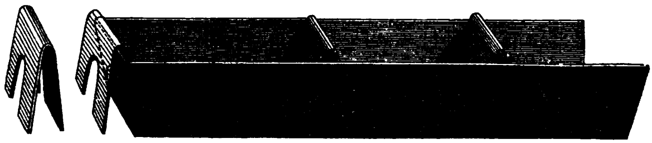


Fig. 90.

of the furnace. To confine the fire to particular portions of the tube, two screens are employed, seen in their places in the figure. The openings in these screens must be sufficiently large to receive the analysing-tube without difficulty; a screen is placed at the anterior part of the furnace during the combustion, to protect the cork of the tube from the heat of the coals. The furnace is placed, during the combustion, on a large tile, resting on a block of wood, a wedge being thrust between the tile and the wood, to give the air free access to all the holes of the grating, or it may be placed on an iron tripod, as shown in Fig. 93.

(e.) *Charging the Combustion Tube.*—A sheet of clean glazed paper being laid on the table, the cork is removed from the combustion-tube, and warm oxide of copper introduced to about *a* (Fig. 86), this serves as a measure for the quantity required for the analysis; it is shaken from the tube into a clean warm porcelain mortar, which should have a rough or unglazed bottom, as rendering the mixture less liable to adhere to it; about an inch of oxide is left at the end of the tube. The substance to be analysed is now shaken from the little stoppered bottle, in which it has been weighed, into the oxide in the mortar, and the whole is gently, but well mixed together with the pestle. The incorporation being complete, the mixture is transferred from the mortar to the tube, which is best done by depressing

the open extremity into the mixture, and turning the tube round; the portions which cannot in this way be got into the tube, are poured on a smooth glazed card, and thus introduced. The mortar is now rinsed out with a fresh quantity of warm oxide, which is also transferred to the tube, and which will occupy the space from *a* up to about *b*; lastly, the tube is filled to within an inch of the end with pure oxide from the crucible. The distribution of the mixture in the tube is therefore as

Fig. 91.

follows:—From the extremity to *c*, pure oxide; from *c* to *a*, the mixture of oxide and the organic substance; from *a* to *b*, rinsings of the mortar; and from *b* to *d*, pure oxide. The process of filling the tube should be completed before the oxide of copper has got cold. The cork is now put in its place, and the tube being grasped between the forefinger and thumb of each hand, is tapped smartly a few times on the table, so as to shake together the contents, to free the pointed extremity entirely from oxide, and to have a channel above the mixture from end to end, to allow of the escape of the gaseous products of decomposition which would otherwise force the mixture from the tube. Fig. 91 shows the tube as it should appear with the mixture shaken into its place. Now, as during the process of

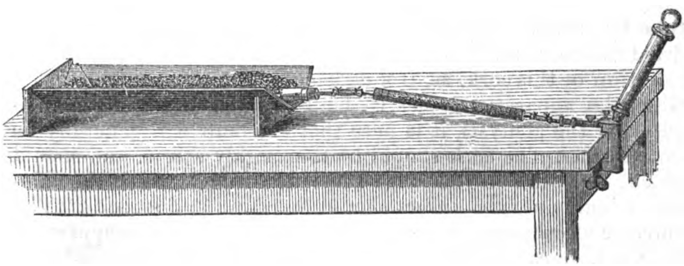


Fig. 92.

mixing, the oxide of copper may have absorbed aqueous vapour from the air, and as this moisture would vitiate the results of the analysis, by giving too high a number for the hydrogen,

the next step of the operation is to get rid of the moisture, which is done by placing the tube in a wooden trough and covering it with hot sand, the temperature of which should be above 212°, but not sufficiently high to char paper. To facilitate the removal of the aqueous vapour, the air is exhausted from the tube, while it is surrounded with the hot sand, by means of a small exhausting syringe, as shown in Fig. 92 ; after a few strokes of the piston the stopcock is opened, by which fresh air is admitted, which becomes completely dried by passing through a chloride of calcium tube. This process of alternate exhaustion and readmission of air, is repeated ten or a dozen times, and the absence of all hygroscopic moisture is thereby ensured.

(f.) *Arrangement of the Apparatus for the Combustion.*—This will be perfectly understood from an inspection of Fig. 93.

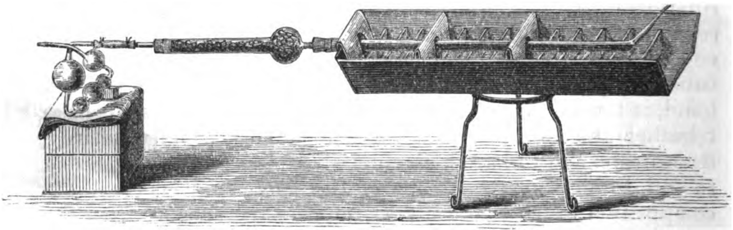


Fig. 93.

The chloride of calcium tube is connected with the combustion tube by means of a perforated cork, which has been thoroughly dried in the water bath; the operator must be careful in the selection of this cork, as, if a deficiency of tightness is detected when the apparatus comes to be examined previous to commencing the analysis, it is here that the fault will generally be found to lie. The cork should be thoroughly sound, and should be cut smooth and tapering; the hole through which the chloride of calcium tube enters should be round and smooth. The chloride of calcium tube is connected with the potassa apparatus by a double caoutchouc tube secured by strong silk cord; the caoutchouc should be soft so as to yield to the pressure of the cord, which should be tied in a bow, and not in a knot, in order that it may be readily removed at the end of the analysis. It will be noticed that it is the extremity of the potassa apparatus, in connection with the *large* bulb which is attached to the chlo-

ride of calcium tube. The combustion tube should project a full inch from the end of the furnace, the screen being placed over it to protect the cork, as shown in the figure. The bulbs of the potassa tube rest on a folded towel, or silk handkerchief placed on blocks of wood raised to the requisite height, and the apparatus is inclined slightly by placing a cork underneath one of the side bottom bulbs, as seen in the sketch. The whole arrangement should have a slight inclination forwards, from the sealed end of the combustion tube to the junction of the chloride of calcium tube with the potassa bulbs. The apparatus being thus far disposed, the next step is to see that the junctions are all perfectly air-tight; this is done in the following manner:—A red-hot coal is held near the large side-bulb of the potassa tube, the enclosed air becomes hereby expanded, the ley sinks, and, as the heat increases, a portion of the expanded air escapes in bubbles through the several bulbs,

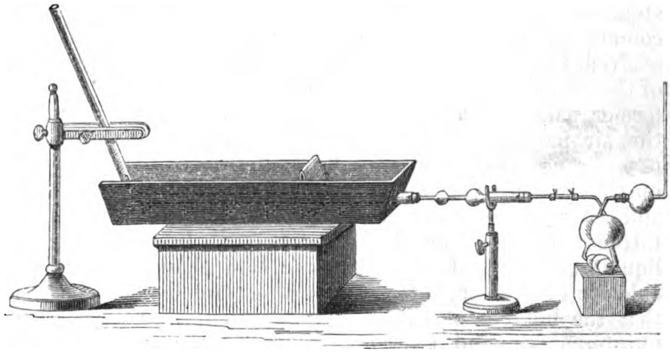


Fig. 94.

out at the open end of the tube; when about a dozen bubbles have in this way been expelled, the hot coal is removed, and the bulbs are set level on the cloth; as the bulb cools, the air remaining in it contracts, and the potassa ley rushes back and fills it more or less. It is now left for a few minutes, during which time the operator may be employed in re-weighing the little bottle which contained the substance about to be analysed; if at the end of five minutes or so the potassa ley should show no disposition to recede from the large side-bulb, and once more take up a horizontal position, it may be concluded that the apparatus is perfectly tight: on the other hand, should

the liquid not preserve the level which it had acquired after the cooling of the large bulb, then the junctions are not tight, and the fault will most likely be found in the cork. Supposing, however, the apparatus to have been proved to be air-tight, the potassa apparatus is once more inclined, and the combustion commenced.

(g.) *Management of the Combustion.*—A good supply of red-hot charcoal being provided close at hand, that part of the tube included between the anterior part of the furnace and the first screen is quickly surrounded with small pieces of hot coal, so as to bring it speedily to a red-heat; the potassa in the large bulb will almost immediately be seen to recede, owing to the expansion of the heated air; the screen is then gradually shifted backwards about an inch at a time, exposing a fresh portion of the tube, which, as before, is surrounded with red-hot charcoal; as soon as the heat reaches the mixture of the organic substance and the metallic oxide, the decomposition of the former commences, carbonic acid and aqueous vapour begin to be evolved, the latter is seen lining the interior of the front part of the chloride of calcium tube in the form of dew, while the former passes into the potassa apparatus, driving forward all the air present in the bulbs. At first, the bubbles appear to pass through the ley without being absorbed; but as the combustion proceeds the absorption is more and more complete, and, after a time, if the substance under analysis be free from nitrogen, only a solitary bubble occasionally breaks through the liquid, nothing put pure carbonic acid passing through the chloride of calcium. The combustion should be so managed that the bubbles of gas shall follow each other in a uniform, uninterrupted, and tolerably rapid stream; and the screen should be gradually moved backwards until the whole length of the tube is surrounded with red-hot charcoal. As soon as the evolution of gas in some degree slackens, the heat is raised by fanning the embers with a piece of pasteboard; if the operation has been managed according to the above directions, and if the mixture of the organic substance with the oxide of copper has been thoroughly made, the gas generally ceases suddenly. On this taking place, the cork is removed from underneath the small side-bulb of the potassa apparatus, and the latter laid level on the cloth. The alkaline ley soon begins to recede, slowly at first, but, when it reaches the large bulb which is left at the end of the combustion full of carbonic acid, it rushes

rapidly into it; there is no danger, however, of any of the liquid being carried into the chloride of calcium tube if the proper proportion between the bulbs has been observed in the construction of the potassa apparatus. As soon as the operator sees the potassa rushing back into the large side-bulb, he clips off the extremity of the tube with a pair of nippers; this allows air to enter, and the alkaline liquor immediately recedes. The hot coals are now removed from the posterior part of the tube, a long tube open at both ends is held over the broken extremity, either by an assistant or supported by some convenient rest, and the operator, having inclined the potassa bulbs, places a suction tube on the end, and draws a current of air through the whole apparatus; by this means all the carbonic acid and aqueous vapour which remained in the apparatus are swept into the chloride of calcium tube and potassa bulbs. The disposition of the apparatus at this period is shown in Fig. 94.

The analysis is now finished, and it only remains to take the apparatus apart, and, after the lapse of about half an hour, to weigh the potassa apparatus, and chloride of calcium tube, and calculate the results.

(h.) *Calculation of Results.*—The particulars of the analysis of mannite are as follows:—

	Grains.
Weight of the bottle and substance	83·76
Ditto of the bottle and residue	79·64
Weight of substance analysed	4·12
Weight of the potassa apparatus after combustion	586·64
Ditto before combustion	580·65
Weight of carbonic acid produced	5·99
Weight of the chloride of calcium tube after combustion	276·06
Ditto before combustion	273·20
Weight of water produced	2·86

These numbers furnish the data for calculating the percentage composition of the substance. We have proved by the preliminary experiments that there is no nitrogen, sulphur, phosphorus, or inorganic matter present; it is evident therefore that, after deducting from the weight of the mannite submitted to analysis the amount of carbon and hydrogen obtained in the forms of carbonic acid and water, the remainder

must be calculated as oxygen. Let us see what quantities of these several elements we obtain as the result of our experiment. In the chloride of calcium tube we obtain 2·86 grains of water; how much hydrogen, then, in 4·12 grains of mannite. Now, as every 9 grains of water contain 1 grain of hydrogen, we find the quantity contained in 1 grain by the proportion:—

$$\text{As } 9 : 1 :: 1 : x, \text{ or } \frac{9}{1} = \frac{1}{x}, \text{ or } 9 = \frac{1}{x}, \text{ or } x = \frac{1}{9};$$

that is, the amount of water obtained, divided by 9, gives the amount of hydrogen; consequently, $\frac{2·86}{9} = ·31777 =$ the hydrogen in 4·12 grains of mannite; but it is far more convenient to express the amount in percentage parts, thus:—

$$\frac{2·86 \times 100}{9 \times 4·12} = 7·71 = \text{percentage amount of hydrogen.}$$

Again, in the potassa apparatus we have condensed 5·99 grains of carbonic acid; what is the percentage amount of carbon? 22 grains of carbonic acid contain 6 grains of carbon.

$$\text{As } 22 : 6 :: 11 : 3, \qquad \text{As } 11 : 3 :: 1 : x.$$

$x = \frac{3}{11}$; consequently, the quantity of carbonic acid found, multiplied by 3 and divided by 11, gives the amount of carbon; and we get it in percentage parts by multiplying by 300 and dividing by 11 times the quantity of substance analysed, thus:—

$$\frac{5·99 \times 300}{11 \times 4·12} = 39·61 = \text{percentage amount of carbon.}$$

The composition of the mannite, according to the above analysis, is therefore—

Carbon	39·61
Hydrogen	7·71
Oxygen	52·68
	100·00

Construction of a Formula from the percentage composition of a substance.—Although we may not, as in the case of mannite, be able always to determine the atomic weight of a compound, it is an easy matter to ascertain the *relative* proportion of the equivalents of the elements of which it is composed, provided we have before us a correct statement of its percentage composition; in other words, we can, from such data, deduce its

empirical formula; for this purpose we have only to divide the percentage number of each element by its atomic weight, and to reduce the figures obtained to the simplest expression possible; thus, in our experiment with mannite, we have—

$$\frac{39{\cdot}61}{6} = 6{\cdot}601 = \text{equivalent of carbon.}$$

$$\frac{7{\cdot}71}{1} = 7{\cdot}710 = \text{equivalent of hydrogen.}$$

$$\frac{52{\cdot}68}{8} = 6{\cdot}585 = \text{equivalent of oxygen.}$$

Now here the numbers 6·601 and 6·585 are so nearly alike that it is at once evident that in mannite the number of atoms of carbon and of oxygen are the same; and, on considering the above figures, it is seen that the simple numbers with which they best correspond are 6, 7, 6. Let us see, then, how nearly the numbers calculated in percentage parts from the formula $C_6H_7O_6$ agree with the experimental ones:—

		Theory.	Experiment.
C_6	36	39·57	39·61
H_7	7	7·69	7·71
O_6	48	52·74	52·68
	91	100·00	100·00

The coincidence is so close that there can be no doubt that the above formula is the correct one, though we have no way of confirming it by determining the atomic weight of this peculiar kind of sugar. We shall give presently a case in which the *absolute* as well as the relative proportion of the atoms of an organic substance can be determined, and a *rational* formula deduced for it.

Combustion with Chromate of Lead.—Some organic substances cannot be thoroughly oxidized by burning them with oxide of copper, partly, according to Dumas, in consequence of the formation of a small quantity of *carbide of copper*, together with the reduced metal, and partly owing to the deposition here and there of small particles of carbon. With such substances this source of error is sometimes obviated by introducing into the posterior end of the combustion tube some chlorate of potassa, mixed with oxide of copper; this salt, being heated at the end of the combustion, gives off pure oxygen, in which all the combustible matter must be thoroughly oxidized; care must be taken to heat the part of the tube con-

taining the chlorate gradually, so as to avoid a too rapid evolution of oxygen. The same object is attained by employing *chromate of lead* instead of oxide of copper. This substance is admirably adapted for oxidizing purposes, from its yielding up a portion of its oxygen by heat alone, a property not possessed by oxide of copper. Chromate of lead is prepared by precipitating a clear solution of acetate of lead, containing slight excess of acetic acid, by bichromate of potassa, washing the precipitate thoroughly on a linen strainer, drying, and igniting to fusion in a Hessian crucible. The fused mass is pulverized, and kept in a stoppered bottle. By heat, either alone or in contact with an organic substance, it is decomposed into green oxide of chromium and basic chromate of lead. The combustion of an organic body, with chromate of lead, is conducted precisely in the same manner as with oxide of copper. The chromate is finely pulverized, and mixed while warm with the substance; but, as it is not in the least degree hygroscopic, the process of exhausting the analysing-tube while buried in hot sand may be omitted; a narrower tube than that employed with oxide of copper may be used, and the chromate which has served for one experiment may be used again after refusion.

In the case of substances which burn with difficulty, anthracite coals for example, the chromate of lead may be advantageously mixed with about one-tenth of its weight of fused and pulverized bichromate of potassa. Such substances are however best analysed by burning them with oxide of copper in a current of dry oxygen gas.

Mené ('Comptes Rendus,' lvi. 1033) suggests the substitution of melted *chlorate of potassa* for oxide of copper in the analysis of organic substances, by which he thinks that the process is rendered much easier, and the drawbacks arising from the frequent incomplete combustion of the substance arising from insufficient oxygenation and other drawbacks are entirely obviated. His process is as follows:—Into the end of a closed tube of white glass, about 20 inches long, 0·39 inch wide, and 0·039 inch thick, a quantity of chlorate of potassa (melted and pounded) is introduced equal to about three-quarters of an inch; the mixture of the organic substance (about 15 grains) with sufficient chlorate nearly to fill the tube is then poured in in the usual manner; when full, the tube is closed with an amianthus plug, then with a small cork traversed by a small tube for the disengagement of the gases. The tube thus prepared

is suspended by two iron wires, so that it may be free, and within the reach of the operator; then by means of an india-rubber tube it is put in communication with the potassa apparatus and chloride of calcium tube in the ordinary manner. An ordinary spirit-lamp is placed under the tube, beginning to heat near the amianthus plug. The chlorate of potassa melts almost immediately, burning the matter and forming carbonic acid and water, which are disengaged quietly. Though in many cases (when the substance contains much carbon), ignition, and sometimes even deflagration accompanies combustion, yet there is no danger. When the substance is burnt in the place first heated, the lamp is shifted, so as successively to heat the whole length of the tube. The chlorate at the closed end of the tube is heated last, so as to disengage oxygen, and thus take with it all the analysable gases which may remain in the tube. When the operation is presumed to be at an end, the tube is detached from the estimating-apparatus, and all the chloride of potassium is eliminated by washing to make the tube ready for a fresh analysis. An analysis of this kind occupies twenty minutes, and the operation may be carried on at the will of the operator.

(2.) *Analysis of volatile compounds (solid and liquid) not containing Nitrogen.*—The analysis of *waxy* substances, and of volatile organic solids, is performed in tubes which are somewhat longer and wider than those generally employed. The analysing-tube is filled also in a different manner, as it would obviously be inadmissible to triturate volatile substances with hot oxide of copper, and the nature of oily and waxy bodies renders their admixture in the usual manner impracticable. Solid fusible fats, oils, etc., are weighed in a little tube, the size and shape of Fig. 95. The chromate of lead or oxide of copper is introduced, while hot, into a wide thin glass tube, about twenty inches long, or into a copper tube which can be closed air-tight with a brass cap and lead washer, Fig. 96; in this it is allowed to cool; if chromate of lead be the oxidizing agent employed, a layer of about two inches is first introduced into the combustion tube; but, if oxide of copper is to be used, the same quantity of a mixture of chlorate of potassa and oxide is shaken in; the little tube, with its charge of substance, is then dropped into the analysing-tube, and heat applied so as to melt it, and cause

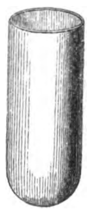


Fig. 95.

it to spread over the lower side; the tube is then filled with the oxidizing agent by introducing its open end within the copper or wide glass tube, containing the oxide of copper or chromate of lead, and turning it round. The tube being filled, the substance to be analysed is diffused through the oxide or chromate by placing it for a few minutes in hot sand, keeping it well corked during the time; the combustion is then proceeded with in the usual manner. If the substance is not of a waxy or fatty nature, it is mixed with the oxide or chromate by means of a copper wire, the end of which is formed like a corkscrew; but the operation requires to be conducted with skill and rapidity.

Fig. 96.

Volatile liquids, such as alcohol, ether, etc., are weighed in two or three small glass bulbs, the size and shape shown in Fig. 97. These bulbs should be drawn out of a long piece of quill tubing, in order to prevent any moisture from getting into them while they are being expanded by the breath. They are filled by heating them slightly over a spirit-lamp, and immersing their pointed extremities in the fluid to be analysed; on cooling, the liquid enters the bulb from the contraction of the heated air, the bulb is again gently heated, on which more air is expelled, and then, on once more dipping the open end into the liquid, an additional quantity enters. In this manner the bulb is about three parts filled with the liquid; upon which its extremity is sealed, and it is weighed, and, the weight of the empty bulb having been previously taken, that of the included liquid is found. The analysing-tube employed should be longer and wider in proportion as the liquid is more volatile. The oxidizing agent is allowed to cool in the closed copper or glass tube, Fig. 96, and, a layer of two inches having been introduced into the combustion tube, the centre of the neck of one of the little bulbs is slightly scratched with a file, the point is quickly broken off, and both bulb and point are dropped into the tube and covered immediately with three or four inches of oxide of copper; another bulb is then introduced in a

Fig. 97.

similar manner, covered with a layer of oxide, and so on with a third, should the substance to be analysed be included in more than two bulbs. The tube is then tapped to open a channel for the escape of the gases.

The analysis of volatile liquids requires a great deal of care on the part of the operator. Thus, if a high heat were suddenly applied to one of the bulbs, a sudden gush of vapour would be produced, a portion of which might either be expelled from the tube without undergoing combustion, or, if it were resolved into carbonic acid and water, these products would be evolved with such impetuosity as to eject the potassa from the bulbs. The greatest care is therefore necessary in conducting the operation. About six inches of the anterior portion of the tube are first heated to redness, and a screen placed behind to prevent the communication of heat to the locality of the bulbs; the fluid in the first bulb is then gently distilled out by holding a red-hot charcoal near it, and the vapour, thus gradually coming into contact with the oxidizing agent, is quietly burned. In this way, the contents of all the bulbs are brought into contact with the heated oxide, and it is advisable to keep a few pieces of hot charcoal against the closed end of the tube, to prevent any of the liquid from distilling back and condensing there.

(3.) *Analysis of organic substances containing Nitrogen.*—The determination of the nitrogen of an organic compound is always an operation distinct from that of the determination of the carbon and hydrogen. It is necessary, however, to modify in some degree the arrangements for the latter process, in the analysis of substances containing nitrogen, or the number for the carbon would always come out too high. The reason of this is that when an organic compound containing nitrogen is burnt with oxide of copper or chromate of lead, a portion of the nitrogen becomes converted into nitric oxide gas, which, on coming into contact with the potassa in the bulbs, is further oxidized into nitrous acid, and is retained by the alkali. It is necessary, therefore, to decompose these oxygen compounds of nitrogen before they can leave the combustion tube; which object is perfectly attained by introducing a layer of four or five inches of fine and pure copper-turnings into the anterior part of the tube and keeping them strongly ignited during the whole analysis. The nitric oxide and nitrous acid are completely decomposed by copper at a high temperature, nitrogen being

evolved in a gaseous form, which passes unabsorbed through the chloride of calcium tube and potassa apparatus.

The copper turnings employed for this purpose must be free from impurities, to ensure which it is advisable to tarnish them by heating them in a crucible, with free access of air, and then to reduce the film of oxide which has formed on their surface by heating them to redness in a glass tube, through which a current of hydrogen is passing.

There are three different ways of estimating the nitrogen of an organic substance, namely, 1st, by collecting the gas in a free state and measuring its volume; 2nd, by determining the relative proportion between the evolved carbonic acid and nitrogen gases; and 3rd, by converting the nitrogen into ammonia, and estimating it as such.

(a.) *Estimation of Nitrogen in a gaseous state.*—This is the method of Dumas, and is applicable to the analysis of all nitrogenous substances, in whatever form that element may exist in them. The substance is burned in the usual way with oxide of copper or chromate of lead; a layer of reduced copper-turnings being placed in the anterior portion of the tube, which should be at least two feet long and not drawn out at the closed extremity, but merely sealed; and from five to eight inches of dry bicarbonate of soda at the posterior end, the object of which is to enable the operator to expel all the atmospheric air from the analysing-tube at the commencement of the operation, and all the nitrogen from it at the end by a current of carbonic acid. The mixture of the substance with the oxidizing agent is made in the manner already described, and the tube filled as shown in Fig. 98; thus, from *a* to *b*, bicarbonate of soda; from *b* to *c*, pure oxide or chromate;

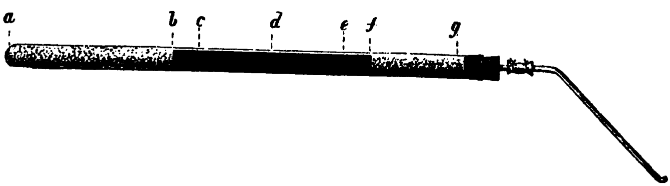


Fig. 98.

from *c* to *d*, the intimate mixture of the substance with the oxidizing agent; from *d* to *e*, rinsings of the mortar; from *e*

to *f*, pure oxide or chromate; and from *f* to *g*, copper turnings. The tube is arranged in the furnace, as shown in Fig. 99, and, the first object being to expel the whole of the atmospheric air, a screen is placed about three inches from the end, and hot coals are applied round the tube before it, so as to heat intensely the bicarbonate of soda, and fill the whole tube with carbonic acid. The conducting tube *c d*, fitted into the combustion tube *a b*, with a good sound cork, passes under the surface of mercury contained in a small pneumatic trough V. The bubbles of gas,

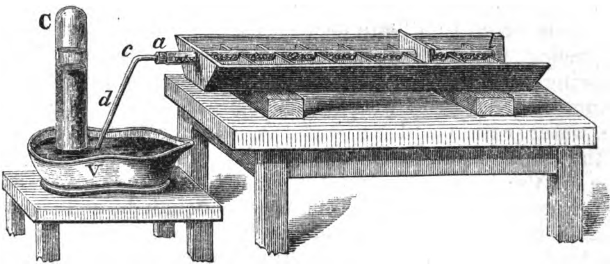


Fig. 99.

as they break through, are received from time to time into a test-tube filled with caustic potassa; and, when they are completely absorbed, it may be concluded that the atmospheric air has been thoroughly expelled from the apparatus. As the success of the experiment depends in a great measure on thus perfectly driving off the air, the operator must not hurry this preliminary process, but continue to apply heat to the bicarbonate of soda till a dozen or so bubbles following are completely absorbed by the caustic ley. A stout glass cylinder *c*, very accurately graduated into *cubic centimètres*, or hundredths of a cubic inch, and of the capacity of about 200 c. c. or 13 c. i., is now filled two-thirds with mercury and one-third with potassa ley and inverted in the pneumatic trough immediately over the conducting-tube *a*;* the combustion is then proceeded

* As caustic potassa acts on the cuticle, making the skin slippery, the best way of filling the cylinder is first to pour in the mercury, then the requisite quantity of potassa ley, and lastly pure water; the jar is then inverted by laying on its edge (which should be ground perfectly smooth) a ground glass plate. If the fingers are allowed to become soiled with the alkali, there will be a danger of the tube slipping through them when the operator is in the act of inverting it in the pneumatic trough.

with in the ordinary manner, the carbonic acid yielded by the decomposition of the substance is absorbed by the ley, while the nitrogen passes into the cylinder in its gaseous form. At the end of the operation, the remainder of the bicarbonate of soda is strongly ignited, and the carbonic acid evolved sweeps the whole of the nitrogen still contained in the tube into the graduated cylinder, while it is itself absorbed by the potassa. The analysis being concluded, the cylinder containing the nitrogen is allowed to remain at rest for some time, to ensure the complete absorption of the carbonic acid; it is then carefully transferred to a large deep glass vessel containing water, by placing underneath its edge the ground glass plate, on removing which under the water the mercury sinks to the bottom of the vessel, its place being supplied by the water. The water within and without the cylinder is then brought to the same level, and the volume of gas read off, the state of the barometer and thermometer being at the same time noted. The analysis is now concluded, and it only remains to calculate the results. The method of doing this will be best understood by quoting the results of an actual experiment.

Weight of substance submitted to analysis, ·600 grm.= 9·264 grains.

Volume of nitrogen gas collected, 41·5 cubic centimètres= 2·531 cubic inches; thermometer, 18·5° Cent.=65·3° F.; barom. 7573 millimètres = 29·9 inches.

Correction of the Gas for temperature.—It is assumed that gases when heated from the freezing to the boiling-point of water, that is, from 0° to 100° of Celsius's thermometer, expand 0·3665, or, in other words, that they expand $\frac{0 \cdot 3665}{100}$ $= 0 \cdot 00366$ for every degree of the Centigrade scale; to find, therefore, what volume the 41·5 cub. cent. of nitrogen observed at 18·5° would occupy at 0°, we must multiply the number of degrees above 0° by the expansion coefficient for one degree, add the product to 1, and divide the observed volume by this sum, thus:—

$$\frac{41 \cdot 5}{1 + (18 \cdot 5 \times 0 \cdot 00366)} = 38 \cdot 87$$ cubic centimètres, the volume the gas would occupy at 0° Cent. This volume has now to be

corrected for pressure; but before doing so, it is necessary to take into consideration *the tension of the aqueous vapour* at the observed temperature: for since the gas was measured in its moist state it must have contained a quantity of vapour of water diffused through it proportional to the temperature, which would counterbalance part of the column of air pressing on the gas; this portion must, therefore, be subtracted from the observed height of the barometer, in order to arrive at the true pressure. In the Appendix will be found a table (extracted from Fresenius's 'Quantitative Analysis'), in which the force of the aqueous vapour at every degree of Celsius from 0° to 40° is expressed in *millimètres*. Referring to this table, it will be found that at the temperature at which the experiment we are now considering was made, viz. 18·5 Cent., the tension of the aqueous vapour amounts to 15·85 millimètres; this, therefore, being deducted from 757·3 millimètres, the observed height of the barometer, gives 741·45 millimètres as the true pressure from which to correct the volume of gas.

Correction of the Gas for pressure.—The normal pressure is assumed to be 760 millimètres (29·9 inches), therefore—
760 : 741·45 :: 38·87 : 37·92 cubic centimètres = the volume of nitrogen corrected for temperature, pressure, and aqueous vapour. The next question is—

What is the weight of 37·92 cubic centimètres of dry nitrogen gas at 0° Cent. and 760· millimètres barom.?

The specific gravity of nitrogen is 0·9706, atmospheric air being unity; and it has been ascertained by careful experiments that 1 litre (1000 cubic centimètres, or 61·03 cubic inches) weighs at 0° Cent. and 0·76 mètre barom. 1·2609 gramme (19·46 grains), therefore:—

$$\text{As } 1000 : 1{\cdot}2609 :: 37{\cdot}92 : x.$$

$x = {\cdot}0478$ grm. (0·738 grains) = the weight of the nitrogen yielded by 0·600 grm. of the substance at the standard temperature and pressure; and—

$$\text{As } {\cdot}600 : {\cdot}0478 :: 100 : 7{\cdot}96$$

= the percentage amount of nitrogen in the substance analysed.

Simpson (Annal. d. Chem. u. Pharm. 95, 74) modifies this process by burning the substance with a mixture of oxide of *copper* and oxide of *mercury*, and sweeping the air out of the tube by a current of carbonic acid, obtained by heating carbonate of protoxide of *manganese* placed in the posterior end of

the combustion tube, instead of bicarbonate of soda. The mixed gases are collected in a pear-shaped receiver of peculiar construction, filled with and inverted over mercury; a little strong solution of caustic potassa being thrown in to absorb the carbonic acid; when the combustion is finished the receiver is detached from the analysing-tube, and the nitrogen is forced into a graduated receiver by the pressure of a column of mercury.

Having thus detailed the general principles of the method of deducing the percentage amount of nitrogen from the volume of gas obtained, we give a formula founded on the above considerations, by which the calculation may be made in a few minutes, and a good deal of trouble saved.

Let v be the observed volume of gas.
B the height of the barometer.
p the tension of aqueous vapour.
t the observed temperature.
m the weight of the substance analysed.

Then,

$$\frac{0{\cdot}12609\, v\, (B-p)}{m\, 0{\cdot}76\, (1+0{\cdot}003665\, t)} \quad \text{or}$$

$$\frac{0{\cdot}1659\, v\, (B-p)}{m\, (1+0{\cdot}003665\, t)} =$$

the percentage amount of nitrogen. If the analysis quoted above as an illustration be calculated according to this formula, the result will be found to be the same as that at which we arrived by the more circuitous method.

(b.) *Estimation of Nitrogen by determining the Relative Proportion between the Carbonic Acid and Nitrogen yielded by the Decomposition of the Substance* (Liebig's method).—This method, which is applicable only to the analysis of substances rich in nitrogen, is performed by burning the substance in the usual way with oxide of copper in a long tube not drawn out at the closed end, and containing at least 5 inches of reduced copper-turnings at its anterior end. After a considerable portion of the substance has been decomposed, and when it is concluded that all the atmospheric air has been expelled from the tube, the evolved gases are collected over mercury in a series of graduated tubes, about a foot long, and half an inch wide. These tubes are then transferred, one at a time, to a tall cylinder (Fig. 100) containing mercury, where the united volumes of carbonic

acid and nitrogen are accurately measured, the mercury within and without the tubes being brought to the same level: a small quantity of potássa ley is then thrown up into the tubes from the siphon (Fig. 101) by gently blowing, the bent extremity being introduced at the open end of the tubes; and after the absorption of the carbonic acid is complete, the residual gas is again measured, the mean result of all the tubes is taken, and the volume of the carbonic acid relative to that of the nitrogen gas, expresses immediately, without any further calculation, the proportion of the equivalents of carbon to those of nitrogen, since one equivalent of carbon is consumed by two equivalents of oxygen, without the volume of the latter undergoing any alteration, yielding therefore two volumes of carbonic acid; and one equivalent of nitrogen yields also two volumes of nitrogen gas.

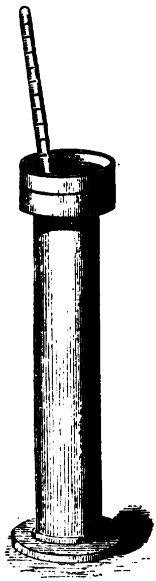


Fig. 100.

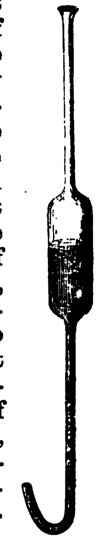


Fig. 101.

The amount of carbon must have been ascertained by a previous experiment; and, that being known, the weight of the nitrogen may be calculated from the atomic weights of carbonic acid and nitrogen: thus, suppose the proportion of carbonic acid to nitrogen to be as 10 to 4, then the compound analysed contains $10 \times 6 = 60$ carbon to $4 \times 14 = 56$ nitrogen. This is the proportion in which these elements exist in uric acid, for the analysis of which this method answers very well; but in cases where the proportion of nitrogen is very small, or where it is evolved in a variable proportion at different stages of the analysis, it is inapplicable, and the method before described, or the one we shall next consider must be adopted.

(c.) *Bunsen's method.*—A stout tube of difficultly fusible glass about 14 inches long, and from half to three-fourths of an inch internal diameter, is drawn out at one end, and then thickened, but not closed in the blowpipe flame. From half to three-fourths of a grain of the substance is well mixed with about 100 grains of oxide of copper, and a small quantity of clean

copper turnings, and the mixture is introduced into the tube, the other end of which is then drawn out so as to allow a space of at least seven inches from *b* to *c*. The tube, thus prepared and filled, has the form shown in Fig. 102. The end *a* is con-

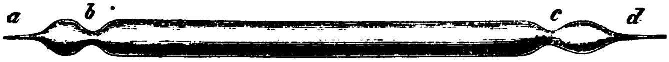


Fig. 102.

nected with an apparatus for generating hydrogen gas, and the end *d* with an exhausting syringe. The gas, previously well dried by passing through strong sulphuric acid, is allowed to flow through the tube until all atmospheric air has been expelled, and replaced by hydrogen gas, which is then rarified by raising the piston of the exhausting syringe, and the tube is immediately closed at *b* by the blowpipe flame. It is then exhausted as completely as possible, and the end *d* closed by the blowpipe flame at *c*. To decompose the substance, the tube is now buried in freshly-prepared gypsum paste laid in a strong iron mould made in two parts, which can be well secured together with bolts, and in which several holes are bored, to allow free issue to the aqueous vapour. As soon as the gypsum has thoroughly set, the mould is slowly heated to bright rednesss in a suitable furnace, and kept at that temperature for about half an hour, it is then allowed to cool, after which the mould is taken apart, the tube is carefully removed from its plaster bed, and the point broken off under a graduated tube filled with and inverted over mercury; a drop of water is previously introduced into the tube, to saturate the moist gas with aqueous vapour. The volume of the gas being taken, due regard being had to the state of the barometer and thermometer, a ball of moistened hydrate of potassa attached to a platinum wire is introduced into the tube, by which the carbonic acid is absorbed; the residual nitrogen gas being dried, by the introduction of a second *unmoistened* ball of hydrate of potassa, its volume is measured, the volume of both gases being reduced to the same temperature, pressure, and dryness, their relative volumes are ascertained, and also the relation of the equivalents of carbon to nitrogen in the substance analysed. This method requires practice and dexterity in the manipulation, but it is, notwithstanding the smallness of the quantity operated upon, susceptible of a high degree of accuracy.

(d.) *Estimation of Nitrogen by converting it into Ammonia.* —This method, which was invented by Drs. Will and Varrentrap, and which is founded on the action of the hydrates of the alkalies on nitrogenous compounds at high temperatures, has already been described (page 273). This process, though accurate, is tedious, on account of the necessity for evaporating the platinum salt on the water-bath, and it is expensive, on account of the alcohol and ether which are required. An important modification of the method was, in consequence of these objections, devised by Peligot ('Comptes Rendus,' March 29, 1847). The combustion is executed in the same manner as in Will and Varrentrap's method, and the ammonia is condensed in a similar bulb apparatus (see annexed cut, Fig. 103), but which, instead of containing hydrochloric acid, is

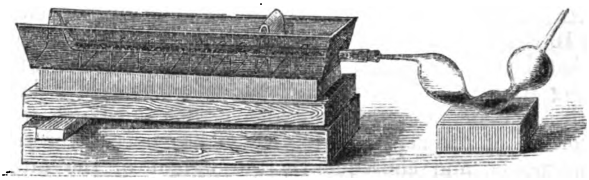


Fig. 103.

partly filled with a fixed weight or volume of sulphuric acid of known strength. Now, as the ammonia which combines with the acid lowers its strength, by determining after the combustion the composition of this liquid, and comparing it with that it previously possessed, it is easy to ascertain the quantity of ammonia that has been condensed, and consequently the amount of nitrogen yielded by the substance submitted to analysis. This operation is executed with as much rapidity as precision, by means of an alkaline solution, likewise of known strength. Peligot recommends a solution of lime in syrup. By triturating slaked lime with a solution of sugar, it dissolves in far greater proportion than in pure water, and the compound formed, possesses the same alkaline reaction as if the base which it contains were free. The operation is conducted as follows:—

A certain quantity of sulphuric acid of known strength is accurately measured into the condensing apparatus. The acid employed by Peligot contains 61·250 grammes of SO_3HO to 1 litre of water; consequently, 100 cubic centimètres corre-

spond to 2·12 grammes of ammonia, or 1·75 gramme of nitrogen. The exact strength of the acid is determined by precipitating an accurately-measured volume with chloride of barium, and determining with the greatest care the quantity of sulphate of baryta produced.

When the combustion is finished, the acid which has served to condense the ammonia is poured into a cylindrical glass, the apparatus carefully washed, and to this liquid, diluted with much water, a few drops of litmus are added to give it a red colour. By means of the solution of lime in sugar, which is contained in a burette graduated in cubic centimètres and in tenths of a cubic centimètre, the acid liquid is accurately saturated, being guided by the blue colour which the liquor suddenly acquires when the point of saturation is attained. The quantity of alkaline liquor required to produce this effect is read off on the burette; and as the amount of the lime compound which saturates 10 cubic centimètres of the normal solution of sulphuric acid has been determined by a previous experiment, by subtracting from this quantity that found for the acid which has absorbed the ammonia from the nitrogenous substance, we find the volume of the acid solution which has been saturated by the ammonia, and consequently the weight of the nitrogen which the body contained.

Shortly after the publication of this method, some experiments to test its accuracy were undertaken by the author (Chem. Gaz., vol. v. p. 411). The substance experimented upon was *vitelline,* a nitrogenous principle extracted from the yolk of the egg. The standard sulphuric acid employed was of the specific gravity 1·0504; the quantity of dry acid which a small bottle of about one cubic inch capacity contained, was very accurately determined by precipitation with chloride of barium, to be 15·8 grains, which agrees exactly with the theoretical amount calculated from the specific gravity by Ure's table. By a simple calculation it was ascertained that this quantity of dry acid is equivalent to 6·715 grains of ammonia, or to 5·53 grains of nitrogen. The solution of lime in sugar was of such a strength that it required 54·25 divisions of the burette to neutralize exactly the bottle full of standard acid. The condensing apparatus employed was larger than it is usually made: it had three bulbs instead of two, and held about two-thirds of the contents of the bottle without being sufficiently full to excite any apprehension of the rushing back of the acid into the combustion tube at the close of the operation.

Example.—7·53 grains of vitelline were burned with soda-lime, and the ammonia condensed in the standard acid, which, after the combustion was finished, was transferred to a beaker, and the apparatus rinsed out repeatedly with distilled water; the remainder of the acid in the bottle was then added, the whole diluted to about half a pint, and a few drops of litmus added; 45 burette measures of the sugar-lime were required to saturate the acid, 9·25 measures (54·25—45) therefore represent the quantity of sugar-lime equivalent to the ammonia given off by the substance; a simple calculation shows this to be equal to 0·941 grains of nitrogen, or 12·5 per cent.

In a second experiment, in which 10·17 grains were burned, 42 measures of the sugar-lime were required to saturate the acid, which gives 12·25 as the representative of the sulphuric acid condensed by the ammonia, and 1·246 grains as the amount of nitrogen = 12·35 per cent.

In a third experiment a different standard acid was employed, and a fresh preparation of vitelline analysed. The acid was equivalent to 4·004 grains of ammonia, or 3·297 grains of nitrogen; and it required for neutralization 32 divisions of sugar-lime, which was also a fresh preparation.

7·24 grains were burned; after the combustion 23·25 measures of sugar-lime were required to saturate the acid; 32 —23·25=8·75 measures represent, therefore, the sulphuric acid neutralized by the ammonia; this gives 0·9016 for the nitrogen in the substance, or 12·45 per cent.

These three experiments agree, it will be observed, very closely with each other. Two experiments, in which the nitrogen was estimated as double chloride of platinum and ammonium, gave 13·02 and 12·6 per cent. of nitrogen, numbers which are rather higher than those obtained by the new method; indeed, from the very principles of Peligot's process, the results must always be a trifle below the truth, it being always necessary to add a slight excess of the alkaline solution, in order to see, by the change of the liquid from red to blue, when neutralization has taken place. It is true that when we are experimenting with a perfectly colourless acid, the smallest addition of the lime solution above that required for the perfect neutralization of the acid immediately determines the blue colour: but, after the acid has served to condense the ammonia produced by the combustion of an animal substance with soda-lime, it is always more or less coloured; nor can a considerable tinge

of yellow be prevented, although it may be much diminished, by using a long combustion-tube and a great excess of soda-lime: this colour renders it somewhat difficult to hit the precise moment when neutralization takes place; if the sugar-lime be added till the liquor becomes distinctly blue, a deficiency of nitrogen amounting nearly to 1 per cent. may easily occur, and it is only practice that will enable the operator to stop exactly at the proper time. The best practical rule is, to use a long combustion-tube, to keep its anterior portion very hot, and to dilute the acid considerably with water previous to adding the alkaline solution. One great advantage which the method of Peligot possesses over all others, is the saving of time which it effects, as by it, a nitrogen determination may be executed in less than half an hour with as much accuracy as by the other methods which require at least three hours.

This process is equally applicable to the analysis of substances which are not very rich in nitrogen, as wheat, vegetable soil, etc., provided a sufficient quantity of the substance be employed. It has been objected that the sugar solution does not keep, but if air be perfectly excluded it remains clear for a considerable length of time, it may however be replaced by a standard solution of soda, which should be perfectly free from carbonic acid.

For the estimation of nitrogen in manures, and for commercial purposes, where great accuracy is not required, the ammonia produced by burning the substance with soda-lime may be condensed in a solution of *tartaric acid* in strong alcohol. The tube conveying the ammonia must not be allowed to dip into the liquid, the receiver containing which, should be provided with a safety tube and connected with a second. The ammonia is collected, and precipitated in the form of bitartrate of ammonia, a salt which is quite insoluble in strong alcohol; it is washed with alcohol on to a tared filter, and dried at about 180° F.; 100 parts of the dried salt contain 10·2 parts of ammonia = 8·4 of nitrogen.

Should the preliminary examination of the organic compound have indicated the presence of *chlorine*, it must be burned with chromate of lead, since, if oxide of copper were employed, a portion of subchloride of that metal would form, and condense in the chloride of calcium tube; and should *sulphur* be present, a tube of perfectly dry *peroxide of lead* must be included between the chloride of calcium tube and the potassa bulbs, in

order to convert into sulphuric acid, and retain as sulphate of lead all the sulphurous acid which may have formed from the oxidation of the sulphur.

The amount of chlorine in chlorinated compounds is determined by igniting them with soda-lime, or by transmitting their vapour through soda-lime, should they be of a volatile nature. The ignited mass is dissolved in dilute nitric acid, and the chlorine determined as chloride of silver. When the organic compound is of an acid nature, Löwig dissolves it in dilute potassa ley, evaporates the solution to dryness, and ignites the residue, by which the chlorine present is converted into a metallic chloride.

207. *Determination of the Rational Formula and Atomic Weight of an Organic Substance:—*

(1.) *Of an Organic Acid.*—An excellent method is to convert it into a silver salt, and to determine accurately the amount of metal which it contains.

Example.—From 0·320 grm. of a certain crystalline substance having acid properties, there are obtained 0·825 grm. of carbonic acid, and 0·1715 grm. of water. Another portion of the acid is exactly neutralized with ammonia, and the solution mixed with nitrate of silver. A white curdy precipitate falls, which is washed on a filter with cold water, and purified by two or three crystallizations out of boiling water; 0·334 grm. of this new substance, being ignited, yields 0·1485 grm. of pure silver.

These numbers calculated centesimally give the following as the composition of the acid, and salt:—

Acid.

Carbon	70·31
Hydrogen	5·95
Oxygen	23·74
Hydrated acid	100·00

Salt.

Oxide of silver	47·73
Anhydrous acid	52·27
Silver salt	100·00

Now, the atomic weight of oxide of silver is 116, therefore—

$$\text{As } 47{\cdot}73 : 52{\cdot}27 :: 116 : x,$$

$x = 127{\cdot}03$, the atomic weight of the anhydrous acid, and $127{\cdot}03 + 9 = 136{\cdot}03$, the atomic weight of the hydrated acid; and, to deduce from this number the formula of the hydrated acid, we have, first, the proportions—

$$\text{As } 100 : 70{\cdot}31 :: 136{\cdot}03 : x;\ x = 95{\cdot}64$$
$$\text{As } 100 : 5{\cdot}95 :: 136{\cdot}03 : x;\ x = 8{\cdot}09$$
$$\text{As } 100 : 23{\cdot}74 :: 136{\cdot}03 : x;\ x = 32{\cdot}29$$

Then by dividing each of these numbers respectively by the atomic weights of carbon, hydrogen, and oxygen, we have—

$$\frac{95{\cdot}64}{6} = 15{\cdot}94 \text{ for the carbon,}$$
$$\frac{8{\cdot}09}{1} = 8{\cdot}09 \text{ for the hydrogen,}$$
$$\frac{33{\cdot}29}{8} = 4{\cdot}036 \text{ for the oxygen,—}$$

numbers which evidently correspond closely with the formula $C_{16}H_8O_4$, which is, therefore, the rational formula of the acid in question; and which, when calculated in percentage parts, agrees almost exactly with that determined by experiment. Thus—

	Calculation.	Experiment.
C	70·58	70·31
H	5·88	5·95
O	23·54	23·74
	100·00	100·00

(2.) *Of an Organic Base.*—The atomic weights and formulæ of these interesting bodies are best determined by analysing with great accuracy the insoluble double salts which they form with *bichloride of platinum*.

Example.—Hofmann and Muspratt obtained by acting on *nitrotoluide* with sulphuretted hydrogen a crystalline body having basic properties, 0·1955 grm. of which, by combustion with oxide of copper, gave 0·5630 grm. of carbonic acid and 0·1515 grm. of water. A double salt of the hydrochlorate of this base and platinum was formed, 0·4337 grm. of which gave, by cautious ignition, 0·1372 grm. of platinum. Now there is every reason for supposing that this double salt is analogous

in composition to the double chloride of platinum and ammonium—

$$NH_4Cl + PtCl_2,$$

if so, its atomic weight is found from the proportion—
As 0·1372 : 04337 : : 98·68 (the atomic weight of platinum) : x, $x = 311·93$, and by deducting from this number the sum of the atomic weights of one equivalent of bichloride of platinum (169·68) and one equivalent of hydrochloric acid (36·5), we get the atomic weight of the new base, 311·93 − 206·18 = 105·75.

The percentage composition of the base, as found experimentally, is—

Carbon	78·53
Hydrogen	8·61
Nitrogen	12·86
	100·00

from which numbers its empirical formula may be deduced thus:—

$$\begin{aligned} &\text{As } 6 : 78·53 :: 1 : x; \ x = 13·09 \\ &\text{As } 1 : \ 8·61 :: 1 : x; \ x = \ 8·61 \\ &\text{As } 14 : 12·86 :: 1 : x; \ x = 0·918 \end{aligned}$$

or $C_{14}H_9N$, which agrees best with the experimental numbers. Thus:—

C_{14}	84	78·50
H_9	9	8·41
N	14	13·09
	107	100·00

The theoretical number 107 agrees so well with the experimental number 105·75, that there can be no doubt that $C_{14}H_9N$ is the correct formula for the new substance.

Gas as Fuel in Organic Analysis.—For the admirable combustion-furnace in which the source of heat is a mixture of coal gas and atmospheric air, shown in Fig. 104, we are indebted to Hofmann, by whom it is thus described (Journ. Chem. Soc., vol. xi. p. 30):—

"Some years ago, a peculiar clay burner was introduced under the name of *atmopyre*. This burner, shown in Fig. 105, is a hollow cylinder of burnt clay, closed at the top, open at the bottom, and with numerous perforations through the sides. Those which I use are 3 inches high, and of $\frac{7}{8}$ inch exterior, and $\frac{3}{4}$ inch interior diameter. The perforations, of about the

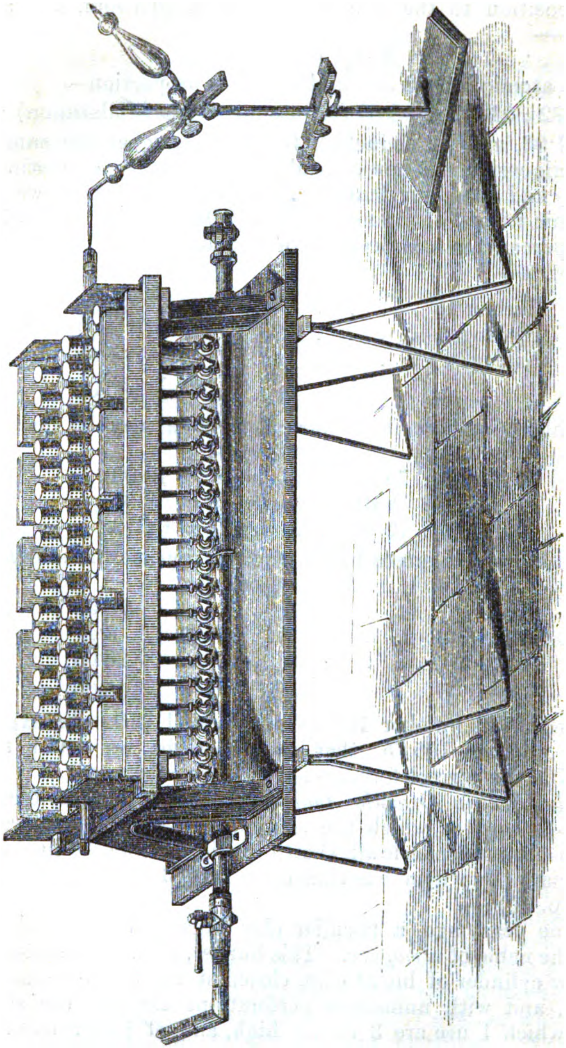


Fig. 104.

thickness of a pin, are made in rows; their number varies, those which I employ have ten rows, each of fifteen holes. From such a clay-cylinder, fixed upon an ordinary bat's-wing burner, the stopcock of which has been appropriately adjusted, the gas burns with a perfectly blue flame, which envelopes the cylinder and renders it in a short time incandescent. These clay-burners are readily obtainable and very indestructible, and by appropriately grouping together a number of them, a complete combustion-furnace for organic analysis may be arranged.

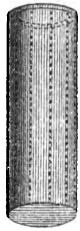


Fig. 105.

"The disposition of the apparatus being obvious from the Fig. 104, a few explanatory remarks will be sufficient. Into a brass tube from 3 feet to 3 feet 8 inches in length (shown in section in Fig. 106) which communicates at both ends with the gas main of the laboratory, there are screwed from twenty to thirty tubes. These tubes, $\frac{1}{2}$ inch thick, and 7 inches high, are provided with stopcocks, and carry brackets of $4\frac{1}{2}$ inches length and $\frac{5}{8}$ inch diameter for the reception of five ordinary bat's-wing burners (each consuming from 3 to 4 cubic feet of gas per hour for a full luminous effect), upon which a corresponding number of clay-burners is fixed. Three of these burners are 3 inches high, the other two are only $1\frac{7}{8}$ inches high, and have only seventy or eighty perforations; supports for two combustion-tubes, side by side, are thus provided, which are bedded in channels of heated fire-clay. The system of brackets lying side by side acquires sufficient stability by a strong iron frame which rests upon two firm supports of cast-iron. The iron frame has, moreover, a groove for the reception of moveable side plates of fire-clay; they are of the same height as the high burners, over which they project by about $\frac{5}{8}$ inch in consequence of their resting upon the iron frame; these side plates (which in Fig. 106 are not drawn quite high enough) are intended as supports to covering plates of fire-clay so that during a combustion the whole or part of the burners may be enclosed.

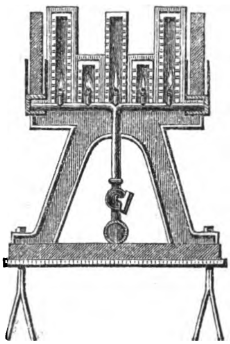


Fig. 106.

"It deserves to be noticed that the efficiency of the furnace

essentially depends upon the correct disposition of the gas-jets. The most appropriate space between the several burners, according to numerous experiments made for the purpose, is about $\frac{1}{8}$ inch. It is very important for the attainment of a perfectly uniform temperature, that the several brackets bearing the burners should be equidistant; their position is therefore specially secured by every bracket being fixed in an aperture formed in the iron frame.

"The use of the furnace scarcely requires any special remark. According to the length of the combustion tube, from eight to ten stopcocks (under all circumstances the largest possible number) are opened at once at the commencement of a combustion. If care has been taken to regulate the amount of gas, either by the stopcocks in the horizontal gas-pipe, or by those in the separate supply tubes, the lighted portion of the furnace in ten or twelve minutes will be in a state of perfect incandescence, comparable only to the ignited mass of charcoal in an ordinary combustion-furnace. After this, it is only necessary to open the remainder of the stopcocks in appropriate succession to ensure a slow and regularly progressing combustion. The time required for the completion of an analysis varies from forty minutes to an hour.

"The heat obtained by this furnace is extremely uniform, and since it is conveyed to the combustion-tube chiefly by radiation from the incandescent mass of surrounding clay, every part of the tube is equally heated. The temperature which it is capable of yielding is entirely at the command of the operator; when strained to its full power, it gives a heat equal to that of the strongest charcoal combustion-furnace. By appropriately adjusting the stopcocks, however, it is possible to maintain the furnace at any desired temperature."

With regard to the quantity of gas consumed by this furnace, Hofmann found that a combustion, lasting one hour, and requiring the whole length of the furnace (34 rows of burners) consumes from 80 to 90 cubic feet. For a carbon determination with 24 rows of burners, which generally lasts about 40 minutes, from 50 to 60 cubic feet are required, and for a nitrogen determination from 25 to 30 cubic feet.

PART III.

SPECIAL METHODS.

CHAPTER X.

ON THE ANALYSIS OF MINERAL WATERS.

208. *Qualitative Analysis.*—The principal constituents are detected *qualitatively* in a brief and simple manner; the rarer substances are most conveniently found in the *quantitative* analysis.

I. *Detection of Carbonic Acid.*—Add to a portion of the water which has been recently collected and kept in a well-stopped bottle, a small quantity of *lime water;* if a precipitate be formed, *carbonic acid* is present.

II. *Detection of Sulphuretted Hydrogen.*—The odour of the water is, in most cases, a sufficient evidence of the presence of this gas, which is confirmed by adding to a small flask, nearly filled with the water, a few drops of solution of acetate of lead, and well agitating; a black precipitate, or a more or less brown coloration of the fluid, indicates sulphuretted hydrogen, or an alkaline sulphide.

III. *Detection of Sulphuric Acid.*—A portion of the water is slightly acidified with hydrochloric acid and gently warmed, chloride of barium is then added; the formation of a white precipitate indicates sulphuric acid.

IV. *Detection of Chlorine.*—A portion of the water is acidified with nitric acid, warmed, and nitrate of silver added; a curdy precipitate, or a turbidity, indicates chlorine.

V. *Detection of Nitric Acid.*—A considerable quantity of the water is evaporated to dryness, the residue is dissolved in a small quantity of water, and tested as directed in section 203.

VI. *Detection of Iodine.*—A large quantity (four or five gallons) of the water is reduced to a small bulk by evaporation,

filtered, and a portion of the filtrate is tested with starch paste and nitric acid as directed in section 199.

VII. *Detection of Bromine.*—Another portion of the residual fluid is treated with chlorine water and ether, as described in section 200.

Detection of Bases.

I. *Detection of Lime.*—Add to a portion of the water, concentrated if necessary by evaporation, oxalate of ammonia, and allow it to stand for a considerable time in a warm place; a white precipitate indicates *lime.*

II. *Detection of Magnesia.*—Concentrate the filtrate from the oxalate of lime, if necessary, by evaporation, and add to the clear residue ammonia and phosphate of soda; the formation, either immediately, or after agitation and rest, of a crystalline white precipitate, indicates *magnesia.*

III. *Detection of Lime in the form of Bicarbonate.*—To a portion of the water, solution of chloride of ammonium is added, and then ammonia; the formation of a white precipitate indicates bicarbonate of lime. Should a notable quantity of iron be present, the precipitate has a more or less yellow tinge; and this is also the case if the water contain organic matter.

IV. *Detection of the Alkalies.*—Should the water contain iron, that metal must be brought to the state of sesquioxide by means of chlorine, it is then precipitated, together with all the other bases but magnesia, by carbonate of ammonia; the further process for the detection of the alkalies is conducted as described in section 159.

V. *Detection of Ammonia.*—A few drops of hydrochloric acid are added to a considerable quantity of the water, which is then evaporated very nearly to dryness at a gentle heat; the residue is tested for ammonia by caustic potassa or by hydrate of lime. Besides the above acids and bases, there are found occasionally in mineral waters the following substances:—*lithia, alumina, strontia, oxides of manganese, zinc,* and *copper,* amongst bases; and *sulphurous, boracic, phosphoric, hydrofluoric,* and *silicic* acids among electro-negative bodies. These bodies are never however found all together in the same water, and as they generally exist in small quantities only, they are, as before observed, best detected in the quantitative examination.

209. *Quantitative Analysis.*—The substances to be estimated may be, amongst bases, *potassa, soda, lithia, ammonia, lime, mag-*

nesia, *strontia*, *alumina*, *oxides of manganese* and *iron;* and amongst electro-negative bodies, *sulphuric*, *phosphoric*, *silicic*, *nitric*, and *carbonic* acids; *chlorine*, *bromine*, *iodine*, *fluorine*, and *sulphuretted hydrogen*, *crenic*, and *apocrenic acids*.

If the operator should have the opportunity of collecting the water himself at the source, he should pay attention to the following particulars:—1st, its temperature as compared with that of the air; 2nd, the geological formation of the locality whence the spring originates; 3rd, the yield of water; 4th, its physical appearance; 5th, whether or not it deposits any solid matter in the pipes or channels through which it makes its exit from the spring or well; 6th, its smell and taste: in short, he should make himself acquainted as accurately as possible with every particular he can obtain with respect to the general history of the water he is about to analyse.

The quantity of water required for a thorough examination is about 12 gallons; if, however, the analyst should have an opportunity of evaporating down a considerable quantity (say 10 *gallons* to 2 or 3 pints) on the spot, for the detection and estimation of those ingredients which only exist in minute quantities, such as *iodine*, *bromine*, *phosphoric acid*, *fluorine*, *oxide of manganese*, *alumina*, *strontia*, *lithia*, and the *organic acids;* or, if he should choose to dispense with a search for these bodies, then a few pints will suffice for a complete analysis of the water for the other ingredients.

I. *Estimation of Carbonic Acid.*—The water for this purpose must be collected at the spring or well by immersing in the water a large pipette of exactly known capacity; four or five stoppered bottles, each of about a pint capacity, should be charged each with one ounce of a strong solution of chloride of calcium and an ounce and a half of ammonia, free from carbonic acid; they should then be filled with the water poured quietly in, to prevent any loss of carbonic acid from splashing; all the carbonic acid contained in the water will thus be precipitated in the form of carbonate of lime. Thus—

$$CaCl + NH_4O + CO_2 = CaO, CO_2 + NH_4Cl.$$

The precipitates in the different bottles, which should be nearly alike in quantity, are collected on a filter, dried at 212°, and weighed. They are then mixed together, and analysed by Fresenius and Will's method (p. 268); the result shows the total amount of carbonic acid in the united volumes of the several bottles of water.

Should the water contain sulphuretted hydrogen, the bottles may be charged with a small quantity of a solution of *arsenious acid* in hydrochloric acid, and the hydrosulphuric acid estimated as *sulphide of arsenic* (p. 443); or the estimation may be made directly in the water by a standard solution of iodine in iodide of potassium (p. 442).

II. *Determination of the Specific Gravity of the Water.*—This is effected in a very simple manner by the method described in page 228. As the specific-gravity bottle has been adjusted with distilled water at 60° F., it is of course necessary that the mineral water should be brought to the same temperature previous to weighing it. The bottle contains exactly 1000 grains of distilled water; the specific gravity, therefore, of the mineral water is exactly as its weight, water being 1000.

III. *Determination of the total amount of Solid Ingredients.*—A quantity of the water (varying from 1000 to 10,000 grains) is carefully evaporated to dryness on the water-bath, the residue is dried at various temperatures, and the weight taken when no further diminution is perceptible. If the water contain any considerable amount of earthy chlorides, and especially if it contain ammoniacal salts, a very exact result cannot in this manner be obtained regarding the amount of the solid contents, for the earthy chlorides retain a small proportion of water at 212°, while, at a higher temperature, some hydrochloric acid may be set free; chloride of ammonium is also partly volatilized at temperatures higher than 212°. If the water do not contain *ammonia, oxide of iron,* or *alumina,* Schweitzer (Mem. Chem. Soc., vol. ii. p. 201), recommends, as a control, to change the carbonates, chlorides, etc., into sulphates, the total amount of which must closely correspond with the amount of the various ingredients when computed as sulphates; this method is indeed applicable when ammonia is present, as that substance being dissipated by heat must be deducted from the total amount of ingredients obtained by analysis. Another method, in cases where great accuracy is desirable, is to evaporate the water with a proportionate quantity of chemically pure anhydrous carbonate of soda sufficient to decompose the earthy chlorides and sulphates. This method of evaporating with carbonate of soda is advantageous, moreover, in preventing the formation of sulphate of lime, which is a troublesome ingredient, inasmuch as it adheres closely to the evaporating vessel, is not readily soluble in dilute hydrochloric acid, and very sparingly soluble in water.

As the solid matters obtained by the evaporation of a mineral water are frequently very deliquescent, the crucible should be cooled underneath a receiver in close proximity to a vessel containing sulphuric acid (p. 247), and weighed as quickly as possible.

The general character of the water having been ascertained by the qualitative examination, the quantitative analysis is proceeded with in the following manner:—

IV. *Estimation of the Sulphuric Acid.*—Ten thousand grains (more or less, according as the preliminary experiment has indicated a greater or less amount of sulphuric acid) are acidified with hydrochloric acid, and precipitated at a boiling temperature by chloride of barium; the precipitate is allowed to settle, then collected on a filter, washed, dried, ignited, weighed, and the amount of sulphuric acid calculated as directed, page 438.*

V. *Estimation of the Chlorine, Iodine, and Bromine* (should the water contain the two latter), *conjointly.*—Two thousand or three thousand grains of the water, according to the quantity of chlorine, etc., supposed to be present, are acidified with nitric acid, the chlorine precipitated with nitrate of silver, and estimated as directed, page 485.

Should the water contain organic matter, it should be freed from it before estimating the chlorine, or it would be partly precipitated, together with the silver-salt, thereby increasing its weight; with this view it should be evaporated with carbonate of soda (perfectly free from chloride of sodium), the liquid filtered from the earthy carbonate precipitated, evaporated to dryness, the residue fused, redissolved in water, nitric acid added, and then precipitated with nitrate of silver. As an illustration of the interference of organic matter with a correct determination of the chlorine, Schweitzer obtained from the Bonnington water, as a mean of several experiments, 10·053 grains of chloride of silver from 4 ounces of the *fresh* water, and 9·694 grains after evaporating it with carbonate of soda, as above described.

VI. *Estimation of the total amount of Lime and Magnesia, Silicic Acid, and Oxide of Iron.*—From 1000 to 10,000 grains of the water are acidified with nitric acid, and evaporated to dryness

* It is better to determine the various ingredients of a mineral water from *weighed* than from *measured* quantities of the water; if the operator have not the advantage of the large balance, Fig. 43, he can employ the specific-gravity bottle, the contents of which, when quite full and the stopper in its place, are known accurately.

at a heat below ebullition. The perfectly dry residue is digested with dilute hydrochloric acid; the silicic acid remains undissolved, having, by the evaporation, been reduced to its insoluble condition. It is separated by filtration, and estimated as directed in section 195. The filtrate which contains the iron, lime, and magnesia in the form of chlorides, is supersaturated with ammonia, by which oxide of iron is precipitated, and is collected and determined as directed in section 169. The lime is thrown down as oxalate, from the filtrate from the oxide of iron, by oxalate of ammonia, and estimated as carbonate or sulphate in the manner described in section 158, and the magnesia is precipitated from the filtrate from the oxalate of lime (concentrated, if necessary, by evaporation) with phosphate of soda, and estimated as pyrophosphate, as directed in section 159.

Schweitzer proceeds in a different manner. He commences with evaporating a large quantity of the water down to a few ounces, together with a proportionate quantity of anhydrous carbonate of soda; he throws the residue on a filter, and lixiviates the solid matter with boiling distilled water till the filtered liquor gives no indications of sulphates and chlorides; he then makes analyses of the soluble and insoluble ingredients separately. The soluble portion contains the alkalies and magnesia in the form of sulphates, chlorides, nitrates, bromides, or iodides; and the insoluble portion contains the earths in the form of carbonates; silica, oxide of iron, oxide of manganese, etc.

VII. *Estimation of the Lime, Magnesia, and Oxide of Iron dissolved in the water by free Carbonic Acid.*—Ten or twelve thousand grains of the water are boiled for some time in a flask, the free carbonic acid is hereby expelled, and the substances which it held in solution are precipitated. The operator must be careful not to allow the volume of the water to be much diminished by the ebullition, or a portion of *sulphate* of lime may be precipitated, together with the earthy carbonates; boiling distilled water should be added from time to time to the flask. The precipitate is collected on a filter, dissolved in hydrochloric acid, a few drops of nitric acid added, and the oxide of iron, lime, and magnesia separated from each other in the usual manner.

Schweitzer dissolves the insoluble matter obtained by his process in nitric acid, evaporates the solution to dryness, and leaves the residue for several hours in contact with nitric acid; he then boils with hydrochloric acid, and, having sepa-

rated the silicic acid, he precipitates the iron by succinate of ammonia. To the filtrate from the persuccinate of iron he adds sulphide of ammonia, which throws down the manganese; he boils the sulphide of manganese with hydrochloric acid, precipitates it with carbonate of soda, washes and ignites the precipitate, which he estimates as *red oxide of manganese.* Having removed the excess of sulphide of ammonium from the fluid filtered from the sulphide of manganese, by boiling it with hydrochloric acid, Schweitzer mixes it in a vessel that can be closed, with ammonia: the precipitate which hereupon forms, he filters quickly, protecting it as much as possible from the air, and having washed and ignited it, he redissolves it in hydrochloric acid. He mixes the solution with bicarbonate of potassa, and, having dissolved the precipitate (should any form) in hydrochloric acid, he boils the solution with caustic soda; if a precipitate should hereby be produced, it is oxide of iron, and must be redissolved in hydrochloric acid and precipitated by ammonia: the caustic ley may contain alumina; to obtain which, it is supersaturated with hydrochloric acid, and precipitated by ammonia. All the magnesia present is retained in solution by the bicarbonate of potassa; to obtain it, Schweitzer neutralizes the fluid with hydrochloric acid, evaporates it quickly with carbonate of potassa, and, when nearly dry, mixes it with boiling water, and filters; he then washes, ignites, and estimates the residue as magnesia. The ammoniacal solution from which the magnesia had been precipitated contains the *lime,* which is precipitated with oxalate of ammonia. The detection of small quantities of manganese in the iron precipitated is best effected by Crum's process, which consists in treating the precipitate with nitric acid, and adding a small quantity of *binoxide of lead.* If manganese be present, the liquid exhibits, as soon as the precipitate has subsided, the magnificent colour of permanganic acid.

VIII. *Estimation of the Lime and Magnesia in the filtrate from the precipitate produced by ebullition.*—They are determined in the usual manner, the lime being first precipitated by oxalate of ammonia, and the magnesia by phosphate of soda. The joint amount of the oxide of iron, lime, and magnesia obtained in the precipitate by boiling, and, in the filtrate, ought to correspond with the total quantity of those ingredients found by the previous experiment.

IX. *Estimation of the Alkalies.*—About 10,000 grains of the

water are evaporated to about one-half, then mixed with excess of baryta water, filtered, carbonate of ammonia added, again filtered, the filtrate evaporated to dryness, ignited, and the alkalies separated from each other, and determined as directed, page 259. If however the water contain a fixed alkaline carbonate, a different plan is adopted. The water is concentrated by evaporation, filtered, and divided into two parts; in one, the amount of chlorine is at once determined by nitrate of silver; the other is evaporated to dryness with slight excess of hydrochloric acid, the residue gently ignited, redissolved in water, and precipitated in its turn by nitrate of silver. The amount of chlorine obtained from this second portion above that obtained from the first, is the equivalent of the quantity of carbonated alkali originally present in the water. Having thus ascertained the amount of carbonated alkali, the total quantity of the alkalies present is found by boiling the water with chloride of barium for some time, and then adding baryta water and filtering; the filtrate is precipitated with carbonate of ammonia, again filtered, and evaporated to dryness; the residue consists of the alkalies in the form of chlorides.

X. *Estimation of the Iodine.*—The filtrate from the precipitate produced by evaporating 10 or 12 gallons of the water down to 2 or 3 pints, is evaporated to dryness, together with carbonate of soda, the residue is digested repeatedly with alcohol, the alcoholic extract evaporated to dryness, and the residue gently ignited in a platinum crucible to destroy the organic matter; it is then dissolved in water and filtered, the clear liquor is carefully neutralized with dilute hydrochloric acid, and then precipitated with protochloride of palladium; the protiodide of palladium, after standing at rest twelve hours, is collected on a filter, washed with warm water, dried at a temperature below 212°, and weighed. For its composition, see page 496.

XI. *Estimation of the Bromine.*—The fluid filtered from the protiodide of palladium is saturated with sulphuretted hydrogen gas, in order to remove the excess of the palladium salt; it is then filtered, boiled with nitric acid, filtered again if necessary, and then precipitated with nitrate of silver; the precipitate which contains all the bromine, together with the chlorine in the form of bromide and chloride of silver, is analysed according to the directions given in section 200. Schweitzer (Phil. Mag., vol. xv. p. 51), having separated the excess of the palladium salt,

evaporates to dryness, redissolves in water, concentrates, and then adds to the solution a few drops of an ammoniacal solution of chloride of silver, prepared by mixing one part of a saturated solution of chloride of silver in ammonia, with one part of ammonia and one of water; this solution, though it produces no turbidity in a saturated solution of chloride of sodium, he finds to indicate a very minute quantity of bromine, which it precipitates as bromide of silver.

XII. *Estimation of the Nitric Acid.*—About a gallon of the water, more or less, according to the amount of solid ingredients, is evaporated with an excess of pure carbonate of soda: the precipitate which is formed is filtered off and washed, the filtrate is evaporated to dryness, and the residue well mixed and weighed; it is divided into two or more parts, each of which may be analysed for nitric acid by Pelouze's method, as modified by Fresenius (page 517). For methods of detecting minute quantities of *ammonia* and *nitric acid* in rain-water, the student is referred to a valuable memoir read at the meeting of the British Association in 1854, by Messrs. Lawes and Gilbert, and to a paper by Dr. E. Pugh (Quart. Journ. Chem. Soc., vol. xii. p. 35).

XIII. *Estimation of the Ammonia.*—A considerable quantity of the water is concentrated by evaporation, having been previously acidified slightly with hydrochloric acid. The concentrated fluid is mixed in a tubulated glass retort with considerable excess of caustic soda, and boiled for a long time, the evolved vapours being condensed in a receiver containing dilute hydrochloric acid, and kept cool by being surrounded with ice or cold water. The boiling having been continued till only two or three ounces of fluid remain in the retort, the distilled fluid is mixed with bichloride of platinum, and evaporated in a porcelain vessel. The dry residue is lixiviated with a mixture of two volumes of alcohol and one of ether, in which the ammonio-chloride of platinum is perfectly insoluble; it is then dried at 212° and weighed: for its composition, see page 272. To control the correctness of the weight, the double salt may be ignited, and the weight of the platinum obtained compared with theory. Schweitzer states that the addition of bichloride of platinum to the distillate previous to evaporating it even at a temperature below 212°, is quite essential to obtaining correct results, inasmuch as *chloride of ammonium* rises with the aqueous vapours,—a fact easily ascertained by covering the vessel during evaporation with filtering-paper, which when lixiviated

will clearly evince the presence of chloride of ammonium, as had been noticed by Berzelius.

XIV. *Estimation of Lithia.*—Should there be reasons for suspecting the presence of this alkali, it must be looked for in the filtrate, produced by evaporating 10 or 12 gallons of the water, about a pound of which should be retained for the purpose. It is boiled to dryness with excess of carbonate of soda; the residue redissolved in water, filtered, and again evaporated to dryness with phosphate of soda; the residue is digested at a gentle heat with water, then ammonia added, and the precipitate (if any) filtered off after standing for some hours: it is washed on the filter with ammonia-water, and dried at a moderate heat. Basic phosphate of lithia ($3LiO, PO_5$) contains 37 per cent. of lithia.

XV. *Phosphoric Acid.*—This is looked for in the precipitate formed by boiling down several gallons of the water. A portion is dissolved in hydrochloric acid, and the phosphoric acid tested for, and estimated as directed in section 193. Another portion of the precipitate may be examined for *iron*, *alumina*, and *manganese*, with which view it is redissolved in hydrochloric acid, and nitric acid having been added to peroxide of iron, the solution is supersaturated with caustic potassa, by which the *iron* and *manganese* are precipitated, and the alumina retained in solution; from the alkaline solution the alumina is precipitated by chloride of ammonium: the mixed oxides of iron and manganese are redissolved in hydrochloric acid, and the oxides separated as directed, page 313.

XVI. *Fluorine.*—This element is to be sought for in the insoluble portion of the saline residue from a considerable quantity of the water. About 500 grains are mixed with a small quantity of pure, finely-divided *quartz*, and boiled for about an hour with concentrated sulphuric acid. If fluorine be present, it is disengaged in the form of *fluoride of silicon*, which is passed into water, the resulting hydrofluosilicic acid is decomposed by ammonia, and the fluoride of ammonium, after separating the silica by filtration, is evaporated, and gently heated in a platinum crucible with concentrated sulphuric acid; hydrofluoric acid is disengaged, which is recognized by its action on glass. Should fluorine be present in some quantity, it will become perceptible at once on passing the fluoride of silicon into water, a flocculent precipitation of silica taking place, which becomes augmented by the addition of ammonia.

XVII. *Estimation of Organic acids* (*Crenic and Apocrenic*).—According to the observations of Mulder, which will be referred to again in the section on the analysis of soils, there exist in the soil at least seven different organic substances, viz. *crenic acid*, *apocrenic acid*, *geïc acid*, *humic acid*, *ulmic acid*, *humin*, and *ulmin;* he divides these substances into two groups—the *humic*, including *geïc acid*, *humic acid*, *ulmic acid*, *humin*, and *ulmin*, and the *crenic*, including *crenic* and *apocrenic* acids; of these bodies *humin* and *ulmin* are insoluble in water and in alkalies, the others are more or less soluble in both; the members of the humic group are precipitated from their alkaline solution by an acid, while *apocrenic* and *crenic* acids are retained in solution; none of these acids contain nitrogen as a constituent element, though they all stand in the closest relation to ammonia, with which they form salts in the soil, and the same is probably the case when the two latter exist in mineral waters.

The *crenic* and *apocrenic* acids are not precipitated from their alkaline solutions by an acid, as above stated. To detect and estimate them in water, therefore, a weighed portion of the precipitate, produced by boiling down some gallons, is boiled for some time with potassa ley, then passed through a filter, acidified with acetic acid, and acetate of copper added; the formation of a brownish precipitate indicates apocrenate of copper, which contains, according to Mulder, about 50 per cent. of apocrenic acid. The fluid filtered from this precipitate is mixed with excess of carbonate of ammonia, and then boiled; if crenic acid be present, a bluish-green precipitate is formed, which, when dried at 284° F., contains, according to Mulder, 74·12 per cent. of oxide of copper.

Besides these organic acids, most mineral waters contain certain other organic matters, which may be determined in the filtrate from the precipitate produced by boiling down a considerable quantity of the water, by evaporating it to dryness with carbonate of soda; the residue is dried at about 284° F., weighed, ignited, and then again weighed: the loss indicates the amount of extracted matter.

XVIII. *Determination of the degree of hardness of natural water* (Clark's process).—By the term *hardness*, as applied to a water, we understand that property which it possesses of decomposing soap, and of forming therewith an insoluble compound. All natural waters possess this property in a greater or less degree,

but practically the hardening constituents are the earthy salts, viz. the carbonates of lime and magnesia, chlorides of calcium and magnesium, sulphate and nitrate of lime, and sulphate of magnesia; the alkaline salts are almost without any effect. Waters which have their origin in chalky soils, where the water charged with carbonic acid percolates through the soil, and readily takes up some of those salts, which are otherwise nearly insoluble, are nearly always very hard; and it is important therefore to ascertain how this hardness may be removed, or at any rate lessened, in the cheapest and most effectual manner. Now the *hardness* of a water may be temporary only, or it may be permanent; if the only earthy salts it contains are the carbonates of lime or of magnesia, or both, they may be removed by simply boiling; but if the water contain *lime* and *magnesia only* in the forms of nitrates, sulphates, and chlorides, it cannot be improved by mere boiling, and its hardness is very difficult to remove; if the water contain earthy salts in the forms of *carbonates*, *sulphates*, *nitrates*, and *chlorides*, then it will have its hardness lessened by boiling, precisely in proportion to the quantity of earthy carbonates which it contains.

We are indebted to Dr. Clark for a very simple method of determining the *degree* of hardness of a water. It consists in ascertaining the quantity of a standard solution of soap in spirit required to produce a permanent lather with a given quantity of the water under examination; the result being expressed in degrees of hardness, each of which corresponds to one grain of carbonate of lime in a gallon (=70,000 grains of distilled water) of the water. From the specification of his patent (enrolled 8th September, 1841), we gather the following particulars :—

(a.) *Preparation of the Soap test.*—Sixteen grains of pure Iceland spar (carbonate of lime) are dissolved (taking care to avoid loss) in pure hydrochloric acid, the solution is evaporated to dryness in an air-bath, the residue is again redissolved in water, and again evaporated, and these operations are repeated until the solution gives to test-paper neither an acid nor an alkaline reaction. The solution is made up by additional distilled water to the bulk of precisely one gallon; it is then called the "standard solution of 16 degrees of hardness." Good London curd soap is dissolved in proof spirit, in the proportion of one ounce avoirdupois for every gallon of spirit, and the solution is filtered into a well-stoppered phial capable of holding 2000 grains of distilled water; 100 test measures, each measure

equal to 10 water grain-measures of the standard solution of 16 degrees of hardness, are introduced. Into the water in this phial the soap solution is gradually poured from a graduated burette; the mixture being well shaken after each addition of the solution of soap, until a lather is formed of sufficient consistence to remain for five minutes all over the surface of the water, when the phial is placed on its side. The number of measures of soap solution is noticed, and the strength of the solution is altered, if necessary, by a further addition of either soap or spirit, until exactly 32 measures of the liquid are required for 100 measures of the water of 16 degrees of hardness. The experiment is made a second and a third time, in order to leave no doubt as to the strength of the soap solution, and then a large quantity of the test may be prepared; for which purpose Dr. Clark recommends to scrape off the soap into shavings, by a straight sharp edge of glass, and to dissolve it by heat in part of the proof spirit, mixing the solution thus formed with the rest of the proof spirit.*

(b.) *Process for ascertaining the Hardness of Water.*—Previous to applying the soap-test, it is necessary to expel from the water the excess of carbonic acid; that is, the excess over and above what is necessary to form alkaline or earthy bi-carbonates: this excess having the property of slowly decomposing a lather once formed. For this purpose, before measuring out the water for trial, it should be shaken briskly in a stoppered glass bottle half-filled with it, sucking out the air from the bottle at intervals by means of a glass tube, so as to change the atmosphere in the bottle; 100 measures of the water are then introduced into the stoppered phial, and treated with the soap test, the carbonic acid eliminated being sucked out from time to time from the upper part of the bottle. The hardness of the water is then inferred directly from the number of measures of soap solution employed, by reference to the subjoined table. In trials of waters above 16 degrees hardness, 100 measures of distilled water should be added, and 60 measures of the soap test dropped into the mixture, provided a lather is not formed previously. If at 60 test measures of soap test, or at any number of such measures between 32° and 60°, the proper lather be produced, then a final trial may

* This standard soap solution, with the burette, mixing-bottle and pipette, for delivering exactly 100 test measures of water, may be obtained of Mr. Griffin, Bunhill Row.

be made in the following manner:—100 test measures of the water under trial are mixed with 100 measures of distilled water, well agitated, and the carbonic acid sucked out; to this mixture soap-test is added until the lather is produced, the number of test measures required is divided by two, and the double of such degree will be the hardness of the water; for example, suppose half the soap-test that has been required correspond to $10\frac{5}{10}$ degrees of hardness, then the hardness of the water under trial will be 21. Suppose, however, that 60 measures of the soap-test have failed to produce a lather, then another 100 measures of distilled water are added, and the preliminary trial made, until 90 test measures of soap-solution have been added; should a lather now be produced, a final trial is made by adding to 100 test measures of the water to be tried, 200 test measures of distilled water, and the quantity of soap test required is divided by 3, and the degree of hardness corresponding with the third part being ascertained by comparison with the standard solutions, this degree multiplied by 3 will be the hardness of the water. Thus, suppose 84·5 measures of soap-solution were required, $\frac{84{\cdot}5}{3} = 28{\cdot}5$, and, on referring to the Table, this number is found to correspond to 14°, which, multiplied by 3, gives 42° for the actual hardness of the water.

TABLE OF SOAP-TEST MEASURES, CORRESPONDING TO ONE HUNDRED TEST MEASURES OF EACH STANDARD SOLUTION.

Degree of Hardness.		Soap-Test Measures.	Differences as for the next Degree of Hardness.
0	(distilled water)	1·4	1·8
1		3·2	2·2
2		5·4	2·2
3		7·6	2·0
4		9·6	2·0
5		11·6	2·0
6		13·6	2·0
7		15·6	1·9
8		17·5	1·9
9		19·4	1·9
10		21·3	1·8
11		23·1	1·8

Degree of Hardness.	Soap-Test Measures.	Differences as for the next Degree of Hardness.
12	24·9	1·8
13	26·7	1·8
14	28·5	1·8
15	30·3	1·7
16	32·0	

When the measures of soap-test necessary to form a lather with 100 test measures of a water exactly correspond with the standard solution, then the degree of hardness will be the corresponding integral number found in the first column. Thus, 24·9 of soap-test will indicate 12° of hardness, 26·7 of soap-test will indicate 13° of hardness, and so on. But if the measures of soap-test do not exactly correspond with a number in the first column, the hardness will be expressed partly by an integer and partly by a fraction. The *integer* will be the hardness corresponding to the next lower number in the soap-test column. The *numerator* of the fraction will be the excess of the soap-test measures in question above this number. The *denominator* of the fraction will be the corresponding difference which follows the soap-test in the next column.

Example.—Let 25·8 be the measures of soap-test required by 100 test measures of a given water; 24·9 is the next lower number in the soap-test column; therefore 12° of hardness, the corresponding degree, is the integral part of the required hardness. The numerator of the fraction is $25{\cdot}8-24{\cdot}9=0{\cdot}9$; the denominator is the corresponding difference$=1{\cdot}8$. Therefore the *fraction* is $\frac{0{\cdot}9}{1{\cdot}8}=0{\cdot}5$, and the whole hardness is 12·5°.

To infer the degree of hardness from an ordinary analysis, Dr. Clark gives the following rule:—Compute the grains of lime, magnesia, oxide of iron, and alumina in a gallon of water each, into its equivalent of chalk; the sum of those equivalents will be the hardness of the water. The experiments of Mr. Campbell, however, show that this rule is not always accurate. He found that water containing sulphate of *magnesia alone* acts towards the soap-test in producing with it a perfect lather, similarly, or nearly so, as water containing a *lime* salt alone, *only* when the equivalent of magnesia salt does not exceed six grains of carbonate lime in a gallon of water. From that point

the magnesian standards begin not to require so much soap-test as the lime, and as the standards increase, this difference in soap-test increases till the magnesian standard of 16° requires only 19·6° soap-tests; whilst the lime standard of 16° requires 32. In standard solutions containing 16°, 12°, 8°, 6°, 4°, 2° lime in a gallon *plus* 1°, 2°, 3°, 4° magnesia, and so on up to 16°, *less* soap-test was requisite to cause a perfect lather in most of the solutions, than is requisite for the standard of lime alone contained in them; or, in other words, the magnesia appeared to *soften* the lime standards, and this peculiarity was found to increase as the magnesia increased. For example,—A standard of lime of 16° takes 32 test measures, a standard of lime 16° + 1° magnesia takes 31·6, and a standard of lime 16° + 16° magnesia takes 27·9. It thus appears that when a water contains both magnesia and lime salts (the former in quantity), the degree of hardness of the water cannot be taken as representing the amount of the earthy salts present; neither can it be considered as giving the amount of lime. It is rarely, however, that a water applicable to domestic use occurs, in which there is such an amount of magnesia present as to occasion serious disturbances in the indications of the soap-test.

Lastly, to obtain uniform results, Dr. Clark recommends that as soon as a lather is formed, such as will remain for five minutes, an *interim* note be taken of the quantity of soap-test used. In about half an hour the bottle should be shaken again, to see whether the lather will still remain for five minutes. If the water does not exceed 4° or 5° of hardness, it is likely to require a little more soap-test upon this renewed shaking; but in every case where more soap-test is required, more must be added. This latter quantity and the former will together make up the whole soap-test.

XIX. *Arrangement of the Results of Analysis.*—The usual method, and the one which seems the most rational (though it must be observed that there is a diversity of opinion on the subject amongst chemists), is to arrange the electro-negative and electro-positive ingredients, as established by direct experiment, into binary combinations, in the ratio of their mutual affinities, the strongest acid being combined with the strongest base, paying attention however to the fact, long since pointed out by Berthollet, viz. that the force of affinity is considerably modified by the degree of solubility of the salts. It is impossible to

lay down any but very general rules for the classification of the results of the analysis of a mineral water, so much depending on the nature of those results, and on various circumstances connected with the history of the water; but, however they are arranged, the direct results obtained in the analysis should be given, and the total amount of the fixed constituents must correspond to the joint amount of the several ingredients; the amounts of the chlorine and sulphuric acid obtained must agree with the joint amounts of the chlorides and sulphates, and the quantity of lime obtained from an evaporated quantity of the water should agree with that obtained jointly from the precipitate produced by boiling a corresponding weight of the water, and from the boiled water filtered from that precipitate.

By way of illustration we append the results of an analysis of the saline water of Purton, lately made by the author (Quart. Journ. Chem. Soc., vol. xiv. p. 48).

Specific gravity of the water at 60° F., 1·0056. Free carbonic acid, 50 cubic inches per imperial gallon, the water being pumped slowly from the well.

Direct Results of Analysis calculated to one Imperial Pint.

Bases.

Experiment.	Lime.	Magnesia.	Alkaline Chlorides.	Chloride of Potassium.	Chloride of Sodium.
I.	6·422	4·748	18·90	1·179	17·721
II.	6·257	4·783	19·33	1·020	18·310
Mean......	6·340	4·765	19·10	1·099	18·016

Acids (or Elements replacing them).

Experiment.	Sulphuric Acid.	Chlorine.	Iodine with traces of Bromine.	Silica.	Carbonic Acid free and combined.	Carbonic Acid as Carbonate of Lime and Carbonate of Magnesia.	Carbonic Acid, free.	Phosphoric Acid.	Apocrenic Acid.
I......	24·00	2·82	„	0·27	„	2·38	„	„	„
II ...	23·80	2·80	„	0·29	„	2·36	„	„	„
Mean	23·90	2·81	0·0094	0·28	5·403	2·37	3·133	0·031	0·112

Verification for Lime.

Experiment.	Lime precipitated by boiling.	Lime left in solution after boiling.	Total by Calculation.	Total by Experiment.
I.	2·282	3·280	6·108	6·422
II.	2·857	3·310	6·077	6·257
Mean	2·842	3·296	6·092	6·340

Verification for Magnesia.

Experiment.	Magnesia precipitated by boiling.	Magnesia left in solution.	Total by Calculation.	Total by Experiment.
I.	0·11	4·735	4·845	4·748
II.	0·15	4·785	4·945	4·783
Mean	0·13	4·755	4·890	4·765

Residue left on Evaporation.

Experiment.	Mineral Residue.	Organic Residue.	Total Residue.
I.	51·02	0·114	51·114
II.	51·21	0·110	51·320
Mean	51·11	0·112	51·217

Solid contents of an Imperial Pint as determined by Analysis.

Carbonate of lime	5·0760
Carbonate of magnesia	0·2630
Lime (not as carbonate)	3·2200
Magnesia (not as carbonate)	4·7580
Potassa	0·6930
Soda	9·5460
Chlorine	2·8100
Sulphuric acid	23·9000
Silica	0·2800

Phosphoric acid	0·0310
Bromine	traces
Iodine	0·0094
Crenic acid	traces
Apocrenic acid	0·1120
	50·6984
Residue left on evaporation	51·2170

Saline Constituents of one Imperial Gallon.

	Grains.
Carbonate of lime	40·608
Carbonate of magnesia	2·104
Sulphate of potassa	10·264
Sulphate of soda	174·904
Sulphate of lime	62·560
Sulphate of magnesia	76·592
Chloride of magnesium	30·000
Iodide of sodium	0·088
Silica	2·080
Phosphoric acid	0·248
Crenic acid	traces
Apocrenic acid	0·896
Bromine	traces
	400·344

XX. *Determination of the Volume of the Gases.*

All water, including even that which has been recently distilled, contains air; if it be desired to collect and estimate the volume of these gases, the process invented by Professor Bunsen may be followed. This consists in expelling the gases by ebullition *in vacuo*, and is conducted in the following manner (Hofmann, Journ. Chem. Soc., vol. vii. p. 166):—

"A globular glass flask, *a*, over the neck of which is fitted a strong vulcanized caoutchouc tube, is immersed in the water until it is filled, and the tube is then closed by means of a brass screw-clamp, which is screwed immediately above the neck of the flask. In this manner a quantity of water is secured which has not been in contact with the air, and the exact volume may be readily determined by experiment. The caoutchouc tube is then connected with a small glass globe, *b*,

partially filled with water, and provided with two necks opposite each other; the one corresponding in diameter to the neck

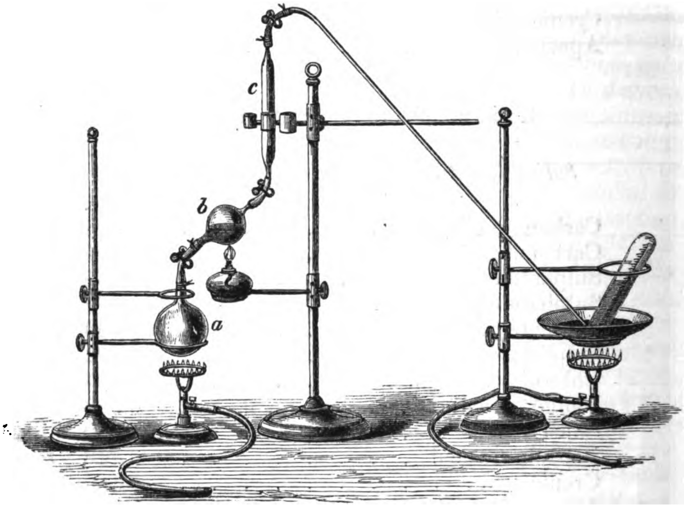


Fig. 107.

of the flask, the other the size of an ordinary quill pen. By the latter, the globular vessel, which may be called the 'boiler globe' may be connected with the glass tube, *c*, about ten inches long and three-quarters of an inch wide, and terminating on each side in a narrow open connecting tube, corresponding in width to the narrow tube of the boiler-globe. The connection of the latter, with the tube which may be termed the 'gas-receiver,' is effected by means of a caoutchouc tube just sufficiently long to admit between the two glass tubes, which are fixed to its ends, the application of a small brass screw-clamp, by means of which arrangement communication between the two vessels may be established or interrupted. In a similar manner the other extremity of the gas-receiver is connected with an ordinary delivery tube, which discharges into water.

"The water flask, *a*, being closed with its screw-clamp, the water in the boiler-globe is heated to ebullition by means of a spirit-lamp, and kept boiling for about a quarter of an hour, by

which time all the air in the apparatus is perfectly replaced by steam, which may be ascertained, moreover, by not a trace of air collecting if the delivery tube be made to discharge for a few minutes under an inverted bell-jar filled with water. The caoutchouc tube at the upper end of the gas-receiver is now closed by a brass clamp, and the spirit-lamp simultaneously removed, when the ebullition *in vacuo* will continue for a considerable time. The boiling out of the water in the flask may now commence. For this purpose the brass clamp is removed, and the flask submitted to a gradually increasing heat. Air bubbles soon make their appearance, but a quarter of an hour generally elapses before the caoutchouc tube, which is collapsed and almost flattened by the atmospheric pressure, is sufficiently expanded to admit of a free communication between the flask and the upper part of the apparatus. The water gradually enters into violent ebullition, in which state it is kept for about an hour, so as to ensure the complete expulsion of every trace of gas. When this point has been reached, the heat is increased for a moment, a good deal of steam is generated in the flask, which causes the water gradually to rise from the boiler-globe into the narrow end of the gas-receiver. At this moment the flask is closed with the clamp, and the source of heat removed; the water in the boiler-globe begins to cool, gradually contracts, and descends in the narrow tube of the gas-receiver; the very moment its level disappears under the caoutchouc connector, the clamp between the boiler-globe and gas-receiver is fastened, and the whole apparatus disconnected. The gas-receiver, closed at both its extremities by caoutchouc, contains the whole of the gas, together with a few drops of water; the volume of the gas may be readily measured by opening one of the clamps under mercury and allowing the metal to enter the gas-receiver until it stands at the same level within and without the tube; the clamp is then secured again, and the mercury transferred into a graduated cylinder. The difference between the volume of mercury and the known capacity of the gas-receiver represents the volume of the gas at the existing barometric pressure and temperature.

The only conditions necessary for the success of this apparently complicated process are a sufficiently long ebullition, and a proper proportion in the capacities of the water-flask and gas-receiver, which can only be attained by a few preliminary operations. The capacity of the gas-receiver must be greater

than the volume of the gas in the water-flask, when measured under the ordinary pressure of the atmosphere. If the volume of the gas were greater, the gas-receiver or the caoutchouc connector might burst, and if they actually withstood the outward pressure, a certain quantity of gas would be lost on opening the clamp under mercury.

CHAPTER XI.

ON THE ANALYSIS OF SOILS.

210. In the examination of soils, the analytical process is divided into two parts:—1. The mechanical analysis; 2. The chemical analysis.

1. *Mechanical Analysis.*

(a.) *Selection of the sample.*—Too much care cannot be taken to obtain a fair average specimen. For this purpose one or two pounds should be taken from each of four or five different parts of the field where the soil appears to be nearly the same. These should be well mixed together, and a pound or so selected for analysis; all samples should be kept in well-corked bottles. It is not unfrequent to see in a field otherwise fertile, a few patches almost barren, where plants, especially when the field is in white crop, spring up, and for a time look quite healthy, but soon become diseased, assume a yellow colour, and die. Specimens from such parts should on no account be mixed with the rest; they should be examined by themselves, and the results compared with those given by the fertile parts: by following this course, the cause of sterility and the means of curing it are most likely to be discovered.

(b.) *Determination of Water.*—Spread a weighed quantity (say half a pound) of the soil upon a sheet of white paper, and expose it to the air in a dry room for several hours, weighing it at intervals of two or three hours till the weight remains constant: the loss indicates the amount of water which has evaporated, but by no means the whole of the water which the soil contains. To determine which, heat about 500 grains of the air-dried soil in a small glass beaker plunged into an oil bath, the temperature of which is kept between 300° and 350° F., till it ceases to lose weight, the result gives a close approxima-

tion to the amount of water. *Absolute* desiccation cannot, however, be accomplished except at a heat close upon redness, which is, of course, inadmissible, as the organic matters the soil contains would thereby become altered or destroyed.

(c.) *Absorbing power.*—Allow the 500 grains of soil dried as above to cool in a covered vessel; then spread it out on a sheet of paper, and expose it to the air for twenty-four hours: note the increase of weight which is due to absorption of water, and if it amounts to ten grains, it is, so far, an indication of great agricultural capability.

(d.) *Power of holding Water.*—Put 1000 grains of air-dried soil into a filter enclosed in another placed in a funnel; pour cold water drop by drop on the soil until it begins to trickle down the neck of the funnel; cover with a piece of glass, and allow it to stand for an hour or two, adding a few drops of water from time to time until it is certain that the whole soil is perfectly soaked; remove the filters from the funnel, and open them upon a linen cloth to remove the drops of water adhering to the paper. The outside filter is now placed in one pan of the balance, and the inner one containing the soil on the other; and the whole being carefully balanced, the true weight of the wet soil is obtained: suppose this to be 1400, then the soil is capable of holding 40 per cent. of water.

(e.) *Rapidity of drying.*—Expose the saturated soil with its filter on the plate to the air, for four, twelve, or twenty-four hours, weighing from time to time. The loss of weight, indicating the tendency of the soil to dry, may convey useful information as to the necessity or otherwise of drainage.

(f.) *Relative proportions of gravel, sand, and clay.*—Rub a quantity of air-dried soil between the hands, and remove and weigh any *stones* which may be present. Weigh off 4000 grains, and pass them through a sieve (No. 1) of copper-wire gauze, the meshes of which are about $\frac{1}{10}$th of an inch in diameter.* Remove the sieve from its bottom, and place it over a deep evaporating basin; throw a gentle stream of water upon the contents, and stir with a spatula or the hand until the water passes through clear. Transfer the residue to another basin, and place it in the water oven to dry; then weigh, after which ignite in the air, and when cold, weigh again. The first weighing gives the amount of *coarse gravel*, and the second indicates the pro-

* Sieves of various degrees of fineness may be obtained at most of the philosophical instrument makers, or they may easily be made.

portion of *organic matter* which this gravel contains. Transfer the soil which has passed through sieve No. 1 to sieve No. 2, the meshes of which are about $\frac{1}{10}$th of an inch in diameter; treat the residue on the sieve precisely as before, dry at 212°, weigh, ignite, and weigh again; the results give the amount of *gravelly sand*, and of organic matter mixed with it. Dry a portion of the soil which has passed through sieve No. 2 in the water oven, and weigh off 500 grains; transfer to a deep basin or flask, and boil for twenty minutes or so, with water. The boiling must be continued until the particles are thoroughly separated from each other. The *coarse sand*, *fine sand*, and *finely divided particles* are then separated from each other by the following simple process, recommended by Schultz:—The boiled soil is allowed to cool, and is then washed into an *elutriating glass*, which is merely a tall champagne glass 7 or 8 inches deep and about 2¾ inches wide at the mouth, round which is fastened a brass ring about half an inch broad, with a tube slightly inclined downwards proceeding from its side. A gentle stream of water is caused to pass continuously into the elutriating glass in such a manner as to cause a constant agitation of the particles, whereby the finest are washed away through the tube at the top of the glass, and received in a beaker or any other convenient vessel. This stream of water is best kept up and regulated by causing it to flow from a reservoir provided with a stopcock, to which is attached a tube funnel from 12 to 18 inches long, drawn out to a point, with a fine aperture. The end of this tube is placed nearly at the bottom of the elutriating glass, and the supply of water so adjusted that the funnel tube always remains half full of water. When the water runs off from the discharge tube nearly clear, the stopcock of the reservoir is closed, and the elutriating glass being removed, the water is decanted from it, and the residue is washed into a small dish, where it is dried and weighed, after which it is ignited and weighed again; the two weights give the proportion of *coarse sand* and its *organic matter*. The elutriated turbid fluid is allowed to stand for several hours, and the water is then poured off into another beaker. The deposited matter, consisting of *fine sand* and *fine soil*, is then subjected to a second elutriating process, conducted as before, except that the force and volume of the washing water is considerably lessened. The operation is continued until the wash water passes off quite clear; this sometimes takes three or four hours, but it is, with the arrangement

we have described, a self-acting process, requiring no personal superintendence. The residue in the elutriating glass is *fine sand*, which, with its organic matter, is estimated as before, by drying, weighing, igniting, and re-weighing. We have only now to deduct from the original 500 grains the quantities of *coarse* and *fine sand*, to obtain the proportion of finely-divided matter. The results of this mechanical analysis may be tabulated thus (Schultz):—

		Fixed Substances.		Combustible Substances.
6·90	Gravel (coarse)	6·90	—	0·00
	Organic matter	..	—	..
7·10	Gravel (fine)	6·43	—	..
	Organic matter	..	—	0·67
35·50	Sand (coarse)	34·37	—	..
	Organic matter	..	—	1·13
40·0	Sand (fine)	38·50	—	..
	Organic matter	..	—	1·50
10·50	Fine soil	9·50	—	..
	Organic and other volatile substances	..	—	1·00
100·00		95·70		4·3

Stones, 2·10 per cent.

This mechanical treatment of soils we deem to be of high importance, and it is to be regretted that so few of our English soils have hitherto been so examined. The same remark applies to the analysis of *clays*, to which the above operations equally apply, except that in the case of clays we have not to look for *gravel*. The following are the results of the mechanical analysis of two clays, one a "fat" and the other a "poor" variety.

	Fat Clay.	Poor Clay.
Coarse sand	6·66	24·68
Fine sand	9·66	11·29
Clay	74·82	57·82
Water	8·86	6·21
	100·00	100·00

These analyses will illustrate the usefulness of the mechanical analysis. To render the matter complete, however, the gravel and sand should be moistened and examined under the microscope with the view of ascertaining if they are wholly siliceous, or if they contain fragments of different kinds of rock, sandstones, slates, granites, traps, limestones, or ironstones. A few drops of strong hydrochloric acid should also be added, when the presence of limestone is shown distinctly by an efferves-

cence; of peroxide of iron by the brown colour which the acid speedily assumes; and of black oxide of manganese by the smell of chlorine, which is easily recognized.

(g.) *Determination of the density of a Soil.*—Dry a sample of the soil (from which the large stones have been picked out) at 212°, in the water-oven, till it ceases to lose weight. Fill a perfectly clean and dry common phial with distilled water up to a mark made with a file on the neck, and weigh it carefully; or the specific-gravity bottle with a long neck (Fig. 44, p. 228) may be used, but it should be of stout glass. Pour out part of the water, and introduce into the bottle in its stead 1000 grains of the dried soil; shake the bottle well to allow the air to escape from the pores of the soil; fill up again with water to the mark on the neck, and again weigh. The weight of the soil divided by the difference between the weight of the bottle with soil and water, and the sum of the weights of the soil and the bottle of water together, gives the density or specific gravity.

Example.	Grains.
The bottle with water alone weighs . .	2000
The dry soil	1000
Sum (being the weight which the bottle with the soil and water *would have had* could the soil have been introduced without displacing any of the water) .	3000
Actual weight of soil and water . . .	2600
Difference (being the weight of water taken out to admit 1000 grains of soil)	400

Therefore 1000 grains of soil have the same bulk as 400 grains of water: that is, the soil is $2\frac{1}{2}$ times heavier than water, since $\frac{1000}{400} = 2{\cdot}5 =$ its specific gravity.

(h.) *Determination of the absolute weight of the Soil.*—Weigh an exact imperial half-pint of the soil in any state of dryness. When this weight is multiplied by 150, it will give *very nearly* the weight of a cubic foot of the soil in that state.

2. *Chemical Analysis.*

Determination of the total quantity of organic substances, volatile Salts, and chemically combined Water.—Having mixed well together the various samples taken from different parts of

the field, allow the mixture to remain for a whole day in the water-oven, then weigh off 1000 grains, and ignite gently in a platinum or porcelain crucible with constant stirring until all blackness has disappeared from the mass, allow it to cool, then drench it with water saturated with carbonic acid, dry, ignite, and weigh. The object of drenching with carbonic acid water is to restore any carbonic acid which may have been expelled by ignition from the chalk which the soil may have contained. Instead of carbonic acid water, a concentrated solution of carbonate of ammonia may be used for this purpose. Pass the ignited soil through sieve No. 2, and submit to analysis the finer particles consisting of clay and sand, weigh off 200 grains, and digest for several hours on the water-bath with excess of a mixture of equal parts of strong hydrochloric acid and water, then add water, and filter into a graduated jar or flask. Wash the residue on the filter with hot distilled water till it passes through tasteless, then break a hole through the bottom of the filter with a stirring-rod, and wash its contents into a small beaker, put it aside for the present, covering it with a glass plate, and marking it (A), calling the hydrochloric solution (B).

Analysis of the Hydrochloric Solution, (B.)—Dilute the solution and washings with distilled water till 100 measures are obtained, well mix by agitation, and divide into four equal parts, I., II., III., IV.

I. *Determination of Sulphuric Acid.*—Heat to ebullition, then add chloride of barium in excess, put aside for twenty-four hours, pour off the clear liquid, transfer the precipitate to a filter, wash, dry, ignite, and weigh 100 parts = 34·31 sulphuric acid. Multiply by 2, the product gives the amount of sulphuric acid in 100 grains of the soil.

II. *Determination of Phosphoric Acid.*—Boil with a little nitric acid to ensure the peroxidation of the iron, then precipitate with ammonia, filter, and having washed the precipitate on the filter, redissolve it in dilute nitric acid. To determine the phosphoric acid in the nitric solution, Fresenius directs to proceed as follows:—dissolve 20 grains of molybdic acid in 180 grains of strong ammonia, mix this with 400 grains of nitric acid, and add the mixture to the nitric solution, digest for twenty-four hours on the water-bath, and wash the precipitate (if any) with the same solution of molybdic acid with which it was produced; let the filtrate stand for some time on the water-bath to see whether a further precipitate will form, and if so,

add this precipitate to the first. Dissolve the precipitate on the filter in ammonia, wash, and agitate the solution well with solution of sulphate of magnesia, the precipitate which is thereby produced is ammonio-phosphate of magnesia. After standing for twenty-four hours it is collected on a filter, and washed with water containing one-sixth of ammonia; it is then dried, ignited, and weighed: 100 parts correspond to 63·96 parts of phosphoric acid. This method, though somewhat troublesome, is accurate. If, however, the operator fail in obtaining any proof of phosphoric acid, he is recommended to repeat the experiment, employing the entire hydrochloric solution of 100 grains of the soil; it is advisable, also, to prepare a considerable quantity of the molybdic solution, as it is employed for washing as well as for precipitation. An important advantage in this method of determining phosphoric acid is, that the presence of alumina and sesquioxide of iron does not interfere with it, it is however, necessary to add the molybdic solution in very considerable excess; and it is inapplicable where the phosphoric acid is in considerable quantity, which is not however likely to be the case in the analysis of soils. Chancel's method, by acid nitrate of bismuth, is stated also to give accurate results. See "PHOSPHORIC ACID."

Schultz recommends the following process:—A considerable quantity of the ignited soil (700 or 800 grains) is digested with hydrochloric acid; the filtrate from the insoluble matter is nearly neutralized by dilute ammonia, taking care not to precipitate permanently the alumina and oxide of iron. To the solution, which should amount to about 1½ pint, 35 to 45 drops of *perchloride of antimony* are added, and set aside for twenty-four hours. A yellowish-white flocculent precipitate is obtained which contains all the phosphoric acid, but it is composed principally of antimonic acid, carrying with it some oxide of iron and alumina, and containing besides a quantity of *ammonia* in proportion to that of *phosphoric acid*. The precipitate well washed with water, is digested with soda-ley containing a certain amount of silicate. After boiling, the liquid is filtered, the oxide of antimony, now changed into antimoniate of soda, remains on the filter with the alumina and oxide of iron. The solution containing the phosphoric acid with a little alumina and silica is supersaturated with hydrochloric acid, then ammonia added; it is concentrated by evaporation, again treated with ammonia, and then filtered. The precipitate of alumina and silica thus obtained carries with it a small quantity of phos-

phoric acid; to remove this, the precipitate is redissolved in a drop or two of hydrochloric acid, the solution is evaporated to dryness, and the residue is warmed with a little acidulated water. After having filtered again to separate the silica, a small quantity of tartaric acid is added to the filtrate, which is then mixed with the preceding ammoniacal solution containing the greater part of the phosphoric acid, which is then precipitated as usual by sulphate of magnesia.

III. *Determination of the Iron.*—All fertile soils contain this metal when in an efficient state of cultivation, as *sesquioxide;* not unfrequently, however, especially where the draining has been neglected, part, and occasionally indeed the whole, of the iron exists as *protoxide.* Now, as the latter oxide is positively injurious, while the former is probably absolutely necessary, it is important to ascertain whether any, and if any, how much of the iron exists in the soil in the form of the hurtful oxide. For this purpose a portion of the fine *non-ignited* particles is extracted with hydrochloric acid, and filtered; the filtrate is nearly neutralized with ammonia, diluted with water, and, if necessary, filtered again; a drop or two of solution of yellow prussiate of potash is added to the clear filtrate. If the precipitate which falls is *dark blue*, the whole of the iron exists as sesquioxide; if the precipitate be *pale blue*, then part at least of the iron is in a state of *protoxide.* Suppose, first, that the whole of the iron exists as sesquioxide, one fourth part of the hydrochloric solution of 200 grains of the soil is transferred to a flask, a little more acid added, and then some small fragments of pure metallic zinc, the flask being placed in a slanting position to avoid any loss, evolution of hydrogen gas takes place, which gradually reduces the iron to the state of protoxide, and the solution at last becomes colourless. The amount of iron is now determined by the volumetric method of Marguerite. It is calculated as sesquioxide (56 iron = 80 sesquioxide), and the amount obtained, multiplied by 2, gives the percentage quantity of sesquioxide of iron in the finely divided matter of the soil. Suppose, however, that the qualitative experiment has shown that some of the iron is in the form of protoxide, in that case a second determination of iron is made in the hydrochloric solution of a weighed quantity of the *non-ignited* fine matter of the soil, *not* previously reducing with zinc, the quantity found is calculated upon 100 grains of the soil, and the result deducted from the total quantity of iron found; the difference gives the proportion of the metal as sesquioxide.

IV. In this portion of the hydrochloric solution, ***silicic acid***, ***alumina***, ***lime***, and ***oxide of manganese*** are determined. It is evaporated to perfect dryness, a little nitric acid being added during the evaporation to peroxidize the iron, the dry and cold residue is sprinkled with hydrochloric acid, and after standing for half an hour, boiling distilled water is poured over it, and it is thrown on a filter; the silicic acid, having by this treatment been rendered insoluble, remains on the filter, on which it is washed, then dried, ignited, and weighed. The filtrate and washings contain the ***oxide of manganese***, ***alumina***, ***lime***, and ***magnesia***, which are separated from each other and estimated as in the analysis of iron ores (see "IRON"). If no oxide of manganese be present, the process may be much simplified. The solution, after the separation of the silicic acid, is at once precipitated by slight excess of ammonia, and filtered as quickly as possible. The precipitate on the filter consists of ***alumina*** and ***sesquioxide of iron***, it is washed, dried, ignited, and weighed. From the weight obtained, that of the sesquioxide of iron already determined is deducted, the remainder is ***alumina;*** the ***lime*** and ***magnesia*** are contained in the filtrate which is treated in the usual manner.

V. *Determination of the Alkalies.*—From 50 to 100 grains of the soil are taken for this purpose, and the method followed is that of Dr. Smith (p. 473), the results are very exact; the fused mass should be digested with *pure water* instead of hydrochloric acid as first recommended by Dr. Smith.

VI. *Determination of Carbonic Acid.*—This is effected on a separate portion of the gently ignited, finer part of the soil by the process of Will and Fresenius. A quantity not less than 100 grains of the soil are introduced into the larger bottle A, Fig. 108, together with a little water; B contains strong sulphuric acid. The upper aperture of the pipette *c*, which is filled with nitric acid, is stopped by a wax plug. The apparatus being accurately weighed, the wax plug is loosened, upon which the nitric acid descends into A, and decomposes any earthy carbonate that may be present, the carbonic acid

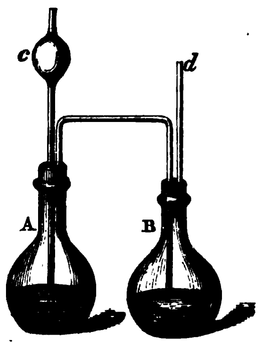


Fig. 108.

evolved escaping through the sulphuric acid in B, and thereby becoming dried. When the effervescence is over, A is warmed, and air is drawn through the apparatus by applying suction at *d*, the wax plug is then replaced, and when cold, the apparatus is re-weighed, the loss of weight indicates the amount of carbonic acid in the form of carbonates in 100 grains of the soil. If the soil be eminently calcareous, the nitric acid must be allowed to flow into the bottle B very gradually.

The Organic Constituents of the Soil.—Mulder ('Chemistry of Vegetable and Animal Physiology,' English Translation) reduces the number of organic substances as at present known to exist in the soil to *seven*. The varieties would indeed be incalculable but for the existence of a general cause which reduces them to a small number. This cause is the transformation and decomposition which vegetables undergo at their death, by which they are converted chiefly into a substance called *humus*. This change is remarkably uniform, since from the innumerable organic combinations which exist in plants and animals, the same few constituents of the black layer of soil are derived; and if we exclude those substances which are mixed accidentally with the black soil, as well as those substances which have not yet undergone sufficient decomposition, its constituents are limited to a small number of organic substances,—substances existing in it everywhere, and on the decomposition of which the growth of plants depends. These substances have the following properties:—Some of them are soluble in water, others in alkalies; others again are insoluble in both, while some dissolve more or less readily in alcohol and ether. The latter are of a resinous nature, and do not appear to have any share whatever in vegetation.

If a soil be exhausted by means of water, a great many salts may be extracted from it, among which may be mentioned the alkalies, lime, magnesia, and ammonia, in combination with *formic*, *acetic*, *carbonic*, *crenic*, *apocrenic*, and *humic* acids. From the soils thus treated with water, alkaline solutions extract substances which may be precipitated by acids. In different kinds of soils the substances thus extracted are sometimes different. They all consist, however, of one or more of the following:—

Geïc acid	$C_{40}H_{12}O_{14}$
Humic acid	$C_{40}H_{12}O_{12}$
Ulmic acid	$C_{40}H_{14}O_{12}$

The latter is that which, in neutral vegetable substances undergoing decay, is formed first. From it, by absorption of oxygen from the air, *humic acid* is produced, and finally, by a further absorption, *geïc acid.* The substances which are insoluble in alkalies, *ulmin* and *humin*, can be rendered soluble, and so converted into *ulmic* and *humic* acids respectively, by the decomposition which is always going on in the constituents of the soil.

The base by which Mulder supposes these acids to be rendered soluble in water is *ammonia.* He does not adopt the idea of Liebig, that this ammonia is carried down to the soil from the atmosphere by means of rain water, but he accounts for its presence in the following manner:—nitrogen in the state of pure gas, and also atmospheric air, are possessed of one common property, namely, that when in contact within an enclosed space with putrefying substances, from which hydrogen is in consequence given off, *the nitrogen combines with the hydrogen, and forms ammonia.* This property of nitrogen is well known. It is the principle on which *saltpetre* is formed, the production of that substance being always preceded by that of ammonia. Now air is contained in the soil, and is in continual contact with moist and decomposing substances. This air could produce saltpetre, if there were only a sufficient abundance of bases, and that even without the presence of putrefying organic substances.

There are in Ceylon numerous natural saltpetre grottos, where there are no organic substances from which nitrogen might be supplied. Nitrogen is derived from the air contained in these caverns, and in favourable circumstances even the water is decomposed, and ammonia at the same time produced, which afterwards is oxidized into nitric acid by the oxygen of the air in places where it has more easy access; this acid then combines again with the bases from the walls of the grottos, and forms nitrates. All this would happen in the soil if organic substances where not present to absorb the oxygen, and thus to prevent the oxidation of the nitrogen in the ammonia, and the formation of saltpetre. In a porous soil in which moist air is contained, nitrogen is combined with the hydrogen of the organic bodies only into ammonia, the oxygen of the water and from the air being consumed in the higher oxidation of the organic substances themselves. In this way the first product of the decomposition of organic substances,

namely *ulmic* acid ($C_{40}H_{14}O_{12}$), is converted into *humic* acid ($C_{40}H_{12}O_{12}$), and this again into *geïc* acid ($C_{40}H_{12}O_{14}$), which in its turn is further oxidized into *apocrenic* acid ($C_{48}H_{24}O_{32}$), and finally into *crenic* acid ($C_{24}H_{12}O_{16}$).

It is to this formation of ammonia from the constituents of atmospheric air and water that we must look, according to the Dutch chemist, for the cause of one of the most important peculiarities in the growth of plants. It is owing to this slow formation of ammonia, that the organic substances of the soil insoluble in water, are rendered soluble, and can be offered to plants as organic food, even without a supply of ammoniacal manure to the soil. In other words, it is owing to this cause that the five acids already mentioned, can be converted into soluble ammoniacal salts. It is particularly worthy of remark, and a fact of great interest, that these humic substances, which can be extracted from the soil by alkalies, and precipitated by acids, have a great uniformity, from whatever kind of soil they may have been prepared; and that they are remarkably similar to those substances which by the action of several chemical agents may be obtained from the materials which are generally diffused through the animal and vegetable kingdoms. The manner in which *sugar* is changed into ulmin, humin, and geïc acid, by a simple transposition of its elements, is thus suggested by Mulder:—

	C.	H.	O.
½ of 7 equivalents of sugar + O_2 .	42	35	37
2 equivalents of carbonic acid . .	2	0	4
19 ditto water	0	19	19
1 ditto *ulmin*	40	16	14
	42	35	37
½ of 7 equivalents of sugar + O_4 .	42	35	39
2 equivalents of carbonic acid . .	2	0	4
23 ditto water	0	23	23
1 ditto *humin*	40	12	12
	42	35	39
½ of 7 equivalents of sugar + O_6 .	42	35	41
2 equivalents of carbonic acid . .	2	0	4
23 ditto water	0	23	23
1 ditto geïc acid . . .	40	12	14
	42	35	41

In the same manner the conversion of *cellulose*, *starch*, *gum*, *pectin*, and other analogous substances, which are so very much diffused through plants, into the humic substances, may be represented; and the way in which his *protein* even may be converted into humic acid, by the influence of hydrochloric acid and oxygen, is shown in a very ingenious manner by Mulder.

The *crenic* and *apocrenic* acids, like the humic acids, exist in the soil in the state of salts of ammonia, potassa, and soda, combined with lime, magnesia, and oxide of iron; they never exist in the soil uncombined. They unite intimately with ammonia, which, however, can be completely separated from them by caustic potassa. *Apocrenic* acid, when artificially prepared, is a *five-basic* acid. It is produced in the form of apocrenate of ammonia when humic acid in whatever way prepared, or wood charcoal, is exposed to the action of nitric acid. Its value in the soil is very highly estimated by Mulder, as in consequence of its *five-basic* character it may supply plants either with several bases at once, or these bases may be alternately exchanged according as the proportion of a more powerful base in the soil is less, and that of a more feeble one temporarily greater; in consequence of these properties he assigns to it a much higher rank than the humic class of acids.

The formation of *apocrenate* of ammonia, by the oxidation of humate of ammonia, is continually going on in the soil during the warmth of summer (except on the very surface which is directly exposed to the air). Each minute portion produced can be taken up by the roots of plants, in the form of double apocrenates of ammonia and various fixed bases, provided there be a sufficient supply of water at hand; and, while in this way the soil loses its apocrenates, a new portion of apocrenate of ammonia is formed from the *humic acid* or *humin*, which is present in large excess. We may thus call the production of apocrenic acid in one respect an organic nitrification.

The series of organic acids present in the soil is, according to the views of Mulder, concluded by a fifth important substance, a final product of the oxidation of organic substances before they are entirely changed into carbonic acid and water, namely, *crenic* acid,* the composition of which is $C_{24}H_{12}O_{16}$. *It* also is combined with ammonia in the soil, and forms double salts which are soluble in water. These exist, along with the apocrenates, in all kinds of water, which have been in contact with organic substances in the soil. They were first found by

Berzelius in spring water; they exist also in the waters of ditches, marshes, and bogs. *Crenic* acid is *four-basic.* By the continual tendency to nitrification in the soil, apocrenic acid must always be converted into crenic acid; the series of *ulmic, humic, geïc,* and *apocrenic* acids thus terminating with *crenic* acid. In the upper layer of the soil, however, where the air is not enclosed, and consequently no tendency to nitrification exists, crenic acid must conversely be changed into apocrenic acid.

Johnston thinks (translation of Mulder's work, p. 184), that to the five acids, mentioned by Mulder, several others may be added, as occurring in certain circumstances in the soil. Thus, from a sample of compressed peat, he extracted by ammonia a substance, from which hydrochloric acid threw down a dark-brown acid, having the composition $C_{24}H_{12}O_{12}$; the same peat, when digested with solution of caustic potassa, or of carbonate of potassa, or carbonate of soda, and precipitated by an acid, gave a substance, having the formula $C_{24}H_{14}O_{9}$; agreeing therefore with the ulmic acid of Mulder, in containing an excess of hydrogen, but not reducible to his ulmic group, the excess of hydrogen being very much greater than in ulmic acid, and the equivalent containing only 24 instead of 40 equivalents of carbon. These acids agree with those of Mulder in their tendency to unite with several bases at once, and to combine with oxygen and nitrogen from the air, producing ammonia, and acids containing more oxygen than the humic and ulmic acids. Again, from a substance called *Pigotite,* found on certain parts of the rocky coasts of Cornwall, where caves occur, Johnston extracted an acid, represented by the formula $C_{12}H_{5}O_{8}$. This acid was obviously formed from the decaying vegetable matter of the soil, and was combined with alumina. It approaches very closely in composition to the *crenic* acid of Mulder, and is called by its discoverer *Mudeseous* acid; on treating its compound with alumina, with nitric acid, Johnston obtained still another acid, the formula of which is $C_{12}H_{5}O_{10}$.

The above is a very brief and imperfect outline of the present state of our knowledge regarding the nature of the organic constituents of the soil. It will be seen that the subject is quite in its infancy, and that no attempt can as yet be made to point out a method of analysing a soil with the view of isolating any particular acid. The following mode of examination must therefore be adopted:—

VII. *Determination of the organic acids of the Humic group.*—Digest 1000 grains of the air-dried soil at a temperature under boiling, with a strong solution of carbonate of soda for several hours; filter, and supersaturate the filtrate with hydrochloric acid. A greater or less quantity of a brown flocculent matter separates; this is collected on a weighed filter, and washed with distilled water till the wash-water begins to be coloured; it is then dried at 212°, and weighed, after which it is burnt, and the weight of the ash (after subtracting the filter ash) deducted from that of the dry mass; the difference gives the *acids of humus.* If a preliminary experiment has shown a considerable proportion of these acids, a smaller quantity of soil may be operated upon.

VIII. *Determination of Humus Coal.*—The soil is boiled for several hours, preferably in a silver dish, with moderately strong solution of caustic potassa, replacing the evaporated water from time to time with distilled water; it is then diluted considerably with water, and filtered. Excess of hydrochloric acid is added to the filtrate, and the precipitated matter collected on a tared filter, washed, dried, and weighed; now, by the action of the caustic alkali, the *humus* coal is converted into *humic* acid, the difference between the weights obtained respectively in this experiment and in the last, expresses therefore the amount of *humus coal.*

IX. *Determination of the total amount of Carbon in a Soil.*—This is effected by burning a known weight of the soil (which has been previously treated with dilute hydrochloric acid, and thoroughly washed) with oxide of copper in an ordinary combustion tube, and receiving the carbonic acid produced, in caustic potassa, contained in an apparatus in which it can be weighed. The increase in the weight of the caustic potassa is due to carbonic acid, derived from the carbon of the organic matter in the soil ($22\ CO_2 = 6\ C$). According to Schultz, 58 parts of carbon correspond on an average to 100 parts of organic matter in the soil. For almost every purpose, the estimation of the total amount of carbon in the manner here indicated is sufficient, and the process is attended with very little trouble. Very little reliance can be placed on the loss of weight which the dried earth suffers by ignition, on account of the tenacity with which some clayey soils retain water.

X. *Determination of the Nitrogen in a Soil.*—Combined nitrogen may exist in a soil in three different forms, viz., as

ammonia, as nitric acid, and as organic matter. If the analysis be intended to be of a rigorous character, it will, of course, be necessary to examine the soil specially both for ammonia and for nitric acid; in almost every case, however, a determination of the percentage amount of nitrogen conveys all the information that is desired on this head. It is effected by burning a known weight of the air-dried soil in a hard glass tube with soda lime (Will and Varrentrapp's process, p. 555).

The ammonia condensed in the acid may be estimated either by a standard alkaline solution, or by converting it into the double chloride of platinum or ammonium. A large combustion-tube is required, it being necessary to burn a considerable quantity of the soil.

XI. *Analysis of the residue* (A) *insoluble in Hydrochloric Acid.*—Evaporate off the water, or draw it off with a pipette; transfer to an evaporating dish, and dry the residue thoroughly on the sand-bath, after which remove it to a platinum or porcelain crucible, and ignite it gently. Digest with excess of sulphuric acid mixed with a little water, until nearly the whole of the acid is driven off (this must be done under a hood). Let the mixture cool, and then add water. Transfer to a filter, and well wash the residue (which will consist generally of pure siliceous sand), dry, ignite, and weigh. The solution containing alumina, with perhaps a little oxide of iron, is precipitated by ammonia, the precipitate is collected on a filter, washed, dried, ignited, and weighed. The weight is entered in the tabular statement of results of the analysis as "alumina not soluble in hot hydrochloric acid."

The accuracy and care with which the whole of these processes have been conducted, is tested by adding together the weights of the several substances that have been separately obtained. If this sum does not differ more than *two* per cent. from the weight of the soil employed, the results may be considered as deserving of confidence. One of the points in which a beginner is most likely to err, is in the washing of the several precipitates. As this is a tedious operation, he is very likely to wash them at first only imperfectly, and thus have an *excess* of weight when his quantities are added together, whereas a small *loss* is unavoidable. The precipitates should always be washed with distilled water, and the washing continued till a drop of what passes through leaves no stain when dried upon a piece of glass.

211. Analysis of Limestones.

The importance of these minerals in agriculture and in the arts, renders the determination of their general composition a matter of frequent occurrence to the practical chemist. The following is the method of procedure:—Dissolve 100 grains of the specimen (which should be well selected and averaged) in dilute hydrochloric acid, and evaporate the solution to dryness on the sand-bath; moisten the residue with hydrochloric acid, let it stand for half an hour, then add boiling distilled water, and filter through a filter which has been previously dried at 212° in the water oven, and weighed; wash on the filter till the wash water passes through tasteless, then return the filter with its contents to the water oven, and dry, until it ceases to lose weight. The increase in weight is the *silicic acid, sand, insoluble clay*, and (perhaps also) *organic matter* in 100 grains of the limestone. It is rarely necessary to do more than determine the total amount of silicic acid in this insoluble residue, which is done by fusing it in a platinum crucible with four times its weight of mixed carbonates of potassa and soda, and evaporating the fused mass carefully to dryness with excess of hydrochloric acid; when perfectly dry it is allowed to cool, then moistened with strong hydrochloric, boiled up with water, and filtered; the residue on the filter is pure *silicic acid;* it is well washed with boiling distilled water, dried, and ignited in a platinum crucible. The crucible should be weighed with its cover on, as silicic acid is apt to take water from the air. In the great majority of cases it is sufficient to determine the *weight* only of the ignited residue of a limestone, insoluble in hydrochloric acid, without submitting it to analysis. The filtrate from the insoluble residue, with the washings, is divided accurately into three equal parts, each part representing one-third of 100 grains of the limestone. One part is mixed in a flask with a little concentrated nitric acid, or chlorine water, to peroxidize any *iron* that may be present, heated nearly to boiling for some time, and then allowed to cool; it is now transferred to a beaker or other convenient vessel that admits of being covered with a glass plate, and ammonia added in slight excess, the precipitate which falls is *alumina* (with a little silicic acid) and perhaps *sesquioxide of iron* and *oxide of manganese;* it is collected on a filter, washed, dried, ignited, and weighed. Except for

scientific (geological) objects, it is rarely necessary to submit this precipitate to analysis. In the filtrate from the precipitate by ammonia, the *lime* and *magnesia* are determined in the usual manner. In order to determine the total amount of carbonic acid, the excellent method proposed by Schaffgottsch may be followed. A known weight of the limestone is heated intensely in a platinum crucible, with four times its weight of recently fused *borax;* the loss of weight when cold, indicates the amount of carbonic acid, *plus* the *water*, which the limestone may contain. The amount of the latter is determined with sufficient accuracy for all practical purposes by keeping 100 grains of the mineral in the air-bath heated to 300°, until its weight is perfectly constant; or the carbonic acid may be determined in a weighed quantity of the limestone finely pulverized, by the process of Will and Fresenius. It will be understood that for mineralogical purposes, the residue insoluble in hydrochloric acid and the precipitate by ammonia must be submitted to minute analysis. If the limestone be intended to be used as a flux (in the iron blast furnace, for example) it may be necessary to examine the residue insoluble in hydrochloric acid for *pyrites;* a portion of it should be fused with a mixture of carbonate of soda and nitrate of potassa; the fused mass digested with dilute hydrochloric acid, and evaporated to perfect dryness; the dry residue moistened with a few drops of hydrochloric acid, then diluted with distilled water, filtered, and the sulphuric acid in the filtrate determined as sulphate of baryta by the addition of chloride of barium.

212. Analysis of Clays.

For technical purposes much information respecting the value of a sample of clay may be derived from a *mechanical* analysis of it (see Analysis of Soils); by this is learnt what are its *compound* parts, how much is *sand*, and how much *clay proper*. The chemical analysis is conducted as follows:—

I. *Moisture, combined water, and organic matter.*—The first, is determined by drying 100 grains of the sample finely pounded, in the water oven, and the two latter, by heating it to redness for a considerable time in a platinum crucible.

II. *Determination of the constituents.*—About 30 grains of the sample are digested for several hours in a platinum crucible with concentrated sulphuric acid; the best method of doing this, is to invert a funnel over the mouth of the crucible, and

place it on a sand-bath underneath a hood. After the digestion has gone on for two or three hours, the funnel is removed, and the greater part of the acid expelled by evaporation; distilled water is now added, and the insoluble residue filtered off, this consists of *silicic acid* (which was probably present in the clay in the form of hydrate) and *sand*. It is boiled two or three times with a strong solution of soda which dissolves the silicic acid and leaves the sand; the alkaline solution is diluted with water, filtered off from the sand, the filtrate supersaturated with hydrochloric acid, and then evaporated to perfect dryness. When cold it is washed on to a filter, and there treated with repeated affusions of boiling water, after which it is dried, ignited, and weighed in a covered platinum crucible; the weight of the sand is also determined after ignition.

The filtrate from the sand and silicic acid, is warmed with a little nitric acid, and then precipitated by slight excess of pure ammonia; it is filtered as rapidly as possible, and the precipitate on the filter consisting of *alumina* and *peroxide of iron* is well washed with hot water; the filtrate may contain *lime* and *magnesia* which are determined in the usual manner. The precipitate of alumina and oxide of iron is dissolved off the filter with hot hydrochloric acid, the filter being thoroughly washed; the filtrate and washings being mixed, are accurately divided into two equal parts, either by weighing or measuring, the former being the most accurate, one half is precipitated by slight excess of ammonia, filtered, and the precipitate washed, dried, ignited and weighed; the weight being calculated for the whole quantity of solution, gives the total weight of *alumina* and *oxide of iron;* the other half of the solution is nearly neutralized with pure carbonate of soda, and then boiled in a silver or porcelain dish with pure caustic potassa, this is repeated twice or even three times, the *alumina* is hereby dissolved and the *sesquioxide of iron* (with perhaps a trace of oxide of manganese) is left behind. The insoluble residue is washed with boiling water, redissolved in hydrochloric acid, precipitated by ammonia, washed, dried, ignited, and weighed; its weight being calculated for the whole solution gives the amount of sesquioxide of iron with sufficient accuracy for most practical purposes; but it is not exact, it being almost impossible to accomplish the perfect separation of *alumina* from *sesquioxide of iron* by caustic potassa. In cases where great accuracy is required, the following method of Rivot may be adopted. The mixed

precipitate of alumina and sesquioxide of iron is ignited and accurately weighed, it is placed in a small porcelain boat, and heated to redness in a porcelain tube, through which a stream of dry hydrogen gas is passing, the oxide of iron is hereby reduced to the metallic state, the alumina remaining unaltered. When no more water is formed, the reduction of the iron is known to be complete, and the tube is allowed to get cold, the current of hydrogen continuing to pass through it; the little boat is then removed, and its contents digested in very dilute nitric acid, which dissolves only the iron, from which it is afterwards precipitated as sesquioxide, by means of ammonia. It is almost needless to observe that this troublesome process is only to be followed in cases where extreme accuracy is required, as in the analysis of minerals for mineralogical purposes. The process recommended (p. 315) may likewise be employed for the separation of these two oxides.

213. Analysis of Manures.

(1.) *Guano.*—The extensive use of this complex manure, its high price, and the consequent inducement held out to unprincipled vendors to sophisticate it, render it a matter of importance that the real value of a sample, as a fertilizing agent, should be capable of being tested, without submitting it to the costly and tedious process of an elaborate analysis. "Impositions," says Professor Johnston ('Elements of Agricultural Chemistry'), "have been practised on unwary farmers, by selling as genuine guano, artificial mixtures, made to look so like guano, that the practical man in remote districts is unable to detect it. A sample of such pretended guano, which had been sown in the neighbourhood of Wigtown, and had been found to produce no effect upon the crops, was examined in my laboratory, and found to contain, in the state in which it was sold, more than half its weight of *gypsum*, the rest being *peat* or *coal ashes*, with a little *common salt*, *sulphate of ammonia*, and either dried *urine*, or the refuse of the *glue* manufactories, to give it a smell. I could not satisfy myself that it contained a particle of real guano." Again, he says, "Four vessels recently sailed hence (Liverpool) for guano stations, ballasted with *gypsum* (plaster of Paris); this substance is intended for admixture with guano, and will enable the parties to deliver from the vessel a nice-looking and light-coloured article. Parties purchasing guano are very desirous of having it delivered from the vessel, as they

believe that they thereby obtain it pure. The favourite material for the adulteration of guano is *umber*, which is brought from Anglesea in large quantities. The rate of admixture, we are informed, is about 15 cwts. of umber to about 5 cwts. of Peruvian guano, from which an excellent-looking article, called African guano, is manufactured."

In selecting a guano the following points ought to be attended to by the farmer, (Anderson, 'Elements of Agricultural Chemistry'):—

1. The guano should be light-coloured and dry, cohering very slightly when squeezed together, and not gritty.

2. It should not have too powerful an ammoniacal smell, and should contain lumps which, when broken, appear of a paler colour than the powder.

3. A bushel should not weigh more than from 56 to 60 pounds.

These characters are, however, imitated with great skill, so that they cannot be implicitly relied upon, and they are applicable to Peruvian guano only. The following are the chief adulterations in guano, which chemical analysis alone can detect:—A sort of *yellow loam*, very similar in appearance to guano, *sand*, *brick-dust*, *chalk*, *umber*, *gypsum*, *common salt*, and occasionally also, ground *coprolites* and inferior guano. These substances are rarely used singly, but are commonly mixed in such proportions as most closely to imitate the colour and general appearance of the genuine article. The adulteration always takes place in large towns, because it is only there that facilities exist for obtaining the necessary materials, and carrying it out without exciting suspicion. "The sophisticated article," observes Anderson, "then passes into the hands of the small country dealers, to whom it is sold with the assurance that it is genuine, and analysis quite unnecessary. In other instances, adulterated and inferior guanos are sold by the analysis of a genuine sample; and sometimes an analysis is made to do duty for many successive cargoes of a guano which, though all obtained from one deposit, may differ excessively in composition. In the case of a Peruvian guano, a complete analysis is not necessary; but an experienced chemist, by the application of a few tests, can readily ascertain whether the sample is genuine. Where the difference in value between different samples is required, a complete analysis is necessary; and this is indispensable in the case of inferior guanos."

Analysis.—The following points should be attended to in the chemical examination of this manure, the sample being mixed as uniformly as possible, and kept in a well-stoppered bottle:—

I. *Determination of the Water.*—Dry 100 grains in the water-oven till it ceases to lose weight. A great difference is here found, even in genuine guanos, the margin extending from 7 to 20 per cent.

II. *Determination of total amount of fixed constituents.*—Incinerate 50 or 100 grains, at a low red-heat, in a porcelain or platinum crucible, till the weight remains constant; the residue (which will, of course, vary greatly according as the guano is ammoniacal or phosphoric) should be white or grey; a yellow or red colour indicates a probable adulteration with *loam*, *brick-dust*, or *sand*.

III. *Determination of the total amount of Ammonia.*—The alkalimetrical method of Peligot, gives excellent results; it involves, however, the operation of distillation. This is obviated by the following modification of the process, which is particularly applicable to the analysis of guano, and ammoniacal manures generally. A weighed quantity (say 20 grains) of the guano is placed in a shallow glass vessel, about four inches in diameter, standing in a plate filled with mercury; on a glass triangle, laid across the dish containing the guano, is placed a second dish, containing a measured volume of standard sulphuric acid; a few drachms of water are then thrown on the guano, and then some milk of lime, by means of a pipette; the whole is now covered with a beaker, and allowed to remain for two or three days, or until reddened litmus-paper is no longer affected when introduced within the glass. The whole of the ammonia has now been expelled from the guano without the aid of heat, and has been absorbed by the acid, the quantity of which left free, is determined by means of a standard solution of soda, and the amount of ammonia calculated from the result.

IV. *Determination of the total amount of Nitrogen.*—The following method, though only an approximative one, recommends itself by the facility with which it is executed, and the rapidity with which it enables the operator to ascertain the comparative values of different specimens of guano. It is founded on the fact, that when guano is treated with a solution of *chloride of lime*, the nitrogen both of the organic matter and of the ammoniacal salts is evolved as gas. Instead of collecting and mea-

suring the gas evolved, which would be scarcely practicable on account of the violent effervescence, the volume of water which is expelled by the gas is ascertained by means of the simple apparatus represented in the figure; it consists of a flask capable of containing about half a pint, provided with a narrow gas delivery tube, bent twice at right angles. One limb, rather the shorter of the two, is passed air-tight through the cork of the flask, and bent upwards, to prevent as far as possible the escape of bubbles of gas. This tube descends nearly to the bottom of the flask. A second very narrow short tube is also passed through the cork, and serves for the escape of air when the cork is introduced. The longer limb of the delivery tube dips into a tall cylinder or tube, which is graduated to cubic centimètres or cubic inches. The flask is half filled with solution of chloride of lime, carefully prepared and kept in a dark place in a closed vessel. About fifteen or twenty grains of guano are then weighed in a small glass vessel which may be the end of a test tube in which a few small shot have been placed in order that it may float. With the aid of the iron-wire handle shown in the figure, the tube is let down so as to float upon the surface of the solution of chloride of lime, the cork with the tube is then tightly adjusted, the orifice of the smaller tube closed with wax, and the flask shaken so that the little vessel may fill and sink; a volume of liquid equal to the nitrogen evolved from the guano, then flows into the graduated cylinder: when no more liquid passes over, the cylinder is depressed so as to bring the liquid to the same level as that in the generating flask. The wax plug is then removed, the cork withdrawn, and the liquid still contained in the delivery tube is allowed to run into the cylinder where the whole is carefully measured. Fifteen grains of good Peruvian guano evolve between four and five cubic inches of gas. A more exact determination of the amount of nitrogen is obtained by burning a known quantity of the manure with soda lime, according to Will and Varrentrapp's method as modified by Peligot (p. 555).

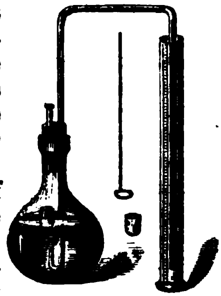


Fig. 109.

v. *Determination of the constituents, soluble and insoluble in Water.*—Digest 150 or 200 grains with several times its volume

of water; throw on a previously dried and weighed filter, and wash till a few drops of the wash-water collected in a test tube are not rendered turbid by the addition of ammonia and chloride of calcium; the filter, with the washed guano, is then thoroughly dried in the water oven and weighed. The difference, less the proportion of water found in (I.) gives the amount of soluble constituents. Burn the insoluble matter and weigh the ash which represents the amount of fixed insoluble salts.

VI. *Sand.*—Dissolve the ash in dilute hydrochloric acid: if it effervesce *strongly*, there is reason to suspect an adulteration of *chalk;* a good guano only gives rise to a slight effervescence. The residue, after being well washed, dried, and gently ignited, is weighed as sand; it should not exceed 2 per per cent.

VII. *Determination of Phosphate of Lime.*—On adding slight excess of ammonia to the hydrochloric solution of the ash, this salt falls; it is filtered off, washed, dried, ignited, and weighed. The filtrate from the precipitate by ammonia should give, on the addition of oxalic acid, only slight indications of *lime.* If, however, a considerable precipitate occurs, the guano has certainly been adulterated with chalk, the amount of which must be determined. Should it be desired to ascertain the exact amount of phosphoric acid, the hydrochloric solution of the ash should be *nearly* neutralized by ammonia, then oxalate of ammonia added, and the solution boiled, acetate of ammonia in excess being added to the boiling liquid. On standing, oxalate of lime precipitates, and is removed by filtration, and the phosphoric acid in the clear filtrate is determined as pyrophosphate of magnesia (sect. 159).

VIII. *Determination of Alkaline Salts.*—For practical purposes it is only necessary to evaporate the filtrate from the phosphate of lime to dryness, and weigh the residue after gentle ignition, to expel the ammoniacal salts, calculating it as "alkaline salts;" when however *chalk* has been found as an adulteration, it must of course be previously removed by oxalic acid.

By way of reference, we append some analyses of the highest and lowest qualities of some *genuine* guanos, on the authority of Professor Anderson ('Elements of Agricultural Chemistry,' p. 210).

	Angamos.		Peruvian.		Bolivian.	
	Highest.	Lowest.	Highest.	Lowest.	Highest.	Lowest.
Water	12·60	7·09	10·37	21·49	11·53	16·20
Organic matter and ammoniacal salts	65·62	50·83	55·73	46·26	11·17	12·86
Phosphates	10·83	8·70	25·20	18·93	62·99	52·95
Alkaline salts............	7·50	16·30	7·50	10·64	9·93	13·83
Sand	3·45	17·08	1·20	2·68	4·38	4·16
	100·00	100·00	100·00	100·00	100·00	100·00
Ammonia	25·33	17·15	18·95	14·65	1·89	2·23

The following is the composition of (so-called) Peruvian guano, which has evidently however been adulterated, and which is worth less than half the price of the genuine manure:—

Water	12·06
Organic matter and ammoniacal salts .	34·14
Phosphates	22·08
Gypsum	11·08
Alkaline salts	12·81
Sand	7·83
	100·00

(2.) *Superphosphate of Lime.*—"The deliberate adulteration of superphosphates," observes Professor Anderson, "that is, the addition to it of sand or similar worthless materials, I believe to be but little practised. The most common fraud consists in selling as pure dissolved bones, articles made in part, and sometimes almost entirely, from *coprolites*. Occasionally refuse matters are used, but less with the intention of actually diminishing the value of the manure, than for the purpose of acting as driers. It is said that sulphate of lime is sometimes employed for this purpose, but this is rarely done, because that substance is always a necessary constituent of superphosphate in very large quantities; and as farmers look upon it with great suspicion, all the efforts of the manufacturers are directed towards reducing its quantity as much as possible."

There is no manure which requires greater vigilance on the part of the purchaser than superphosphate of lime, because of the great variations in quality; though in consequence of increased competition, and the process of manufacture being better understood, it is much better than it was a few years ago.

Analysis.—The following are the points to be attended to in the chemical examination of this manure:—

I. *Determination of the Water.*—50 grains are dried in the air bath at a temperature of about 300° F. until the weight remains constant; the loss represents the amount of moisture absorbed by the superphosphate, and the water in the gypsum.

II. *Determination of the relative proportion of soluble and insoluble constituents.*—150 grains of the sample are boiled up with water, and allowed to settle; the decanted fluid is thrown on a filter, and the residue again and again boiled with water, until there is no longer an acid reaction. The insoluble matter is then dried in the air bath at about 300° F., and weighed. Of course, any solid particles that may have been retained on the filter are added; this is best done by drying and burning the filter, and adding the ash.

III. *Determination of the organic matter in the insoluble portion.*—Moisten with a little nitric acid, to peroxidize any iron that may be present, then ignite at a low red-heat in a platinum crucible, placed sideways, so as to allow air to have access; when cold, weigh. The loss represents the amount of organic matter, *plus* that of any ammoniacal salts that may have been present.

IV. *Analysis of the insoluble matter.*—Boil for some time with dilute hydrochloric acid, dilute largely, and boil again; filter, wash, dry, ignite, and weigh the residue on the filter, which is *sand* and *clay*. Mix the filtrate and washings well together, and divide into three parts—*a*, *b*, *c*. In *a* determine the *sulphuric acid* (from the gypsum) by *chloride of barium;* mix *b* and *c* together, add *oxalate of ammonia*, and considerable excess of *acetate of ammonia*, and boil. All the lime is hereby precipitated as oxalate; it is collected on a filter, and estimated as sulphate. To the filtrate from the oxalate of lime add tartaric acid and ammoniacal sulphate of magnesia,* which precipitates the phosphoric acid as ammonio-magnesian phosphate. Combine the sulphuric acid found in *a* with the quantity of lime requisite to form *gypsum*

* It is convenient to keep on hand a stock of *tartarized ammoniacal*

(40 sulphuric acid + 28 lime); add the remainder of the lime to the phosphoric acid, and enter it as "insoluble phosphate."

V. *Analysis of the soluble portion.* — Divide into three equal parts—*a*, *b*, *c*; transfer *a* to a platinum dish, and evaporate gently on the sand bath, adding, a little at a time, thin *milk of lime*, until a piece of red litmus-paper is turned faintly but distinctly blue, showing an alkaline reaction; continue the evaporation to perfect dryness, transfer to the air bath, dry at 320° F., and then weigh; ignite, and weigh again. The difference between the results of the two weighings expresses the quantity of *organic matter* in the aqueous solution. Boil the ignited residue with lime water, and then with distilled water for a considerable time; remove the sulphuric acid from the filtrate by chloride of barium, and then the excess of the barium and calcium salts by carbonate of ammonia, and filter. The filtrate contains nothing but the *alkalies*, which are determined in the usual manner. Determine the sulphuric acid in *b* by chloride of barium; evaporate *c* to dryness in a platinum dish with excess of carbonate of soda, and add a little nitre; ignite the residue, rinse into a beaker, and dissolve in hydrochloric acid with the aid of a gentle heat. To the clear solution add ammonia, and then *acetic acid* in excess. If any *phosphate of sesquioxide of iron* be here precipitated, filter it off, and divide the filtrate into two equal parts, in one determine the phosphoric acid by the *acetate of protoxide of uranium;* the liquid should be boiled after the addition of this reagent, and the precipitate allowed to subside. Fresenius recommends the addition of a drop or two of *chloroform* immediately after the precipitation, and when the liquid has cooled a little, giving the mixture a vigorous shake, which materially assists the precipitation of the finer particles; these are collected on a filter, the bulk of the precipitate being washed by decantation; the well-washed precipitate is dried and ignited; the filter is also dried and burnt, and its ashes added to the ignited precipitate, 100 parts of which contain 19·78 parts of phosphoric acid.

sulphate of magnesia for phosphoric acid determinations. The following proportions may be used:—

2 pints of		water.
225 grains of		tartaric acid.
80	„	anhydrous sulphate of magnesia.
250	„	chloride of ammonium.

Those engaged in the frequent analysis of superphosphate of lime and other phosphatic manures, will find it convenient to estimate the phosphoric acid by one of the volumetric processes described in section 193. Liebig's method by perchloride of iron, as modified by E. Davy, gives excellent results; on the whole, however, preference must be given to the *acetate of uranium* method (p. 455). Determine the lime and magnesia in the other portion of *c*, in the usual manner.

VI. *Determination of the Nitrogen.*—The process of Will and Varrentrap, as modified by Peligot (p. 555), is to be followed:—

The composition of superphosphates must necessarily vary to a great extent, and depends not only on the materials, but on the proportion of acid used for solution. The following analyses by Dr. Anderson ('Elements of Agricultural Chemistry') illustrate the composition of some good samples made from different substances:—

	Bones alone.		Bone Ash.		Chiefly Coprolites.		Mixtures, containing Salts of Ammonia.	
Water	7·74...	7·79	5·33...	10·40	5·90...	10·17	7·07...	15·82
Organic matter and ammoniacal salts	17·83...	21·69	6·94...	4·92	5·10...	4·13	9·87...	13·96
*Biphosphate of lime	13·18...	9·87	*21·35...	23·09	*12·24...	13·75	*17·63...	12·67
Insoluble phosphates	10·31...	21·17	5·92...	6·08	16·90...	0·17	12·60...	8·40
Sulphate of lime	46·00...	35·30	56·16...	47·78	52·39...	62·62	49·77...	45·14
Alkaline salts	1·46...	0·94	traces		2·47...	0·96	0·06...	1·07
Sand	3·48...	3·24	3·30...	4·30	6·00...	8·20	3·00...	2·94
	100·00...	100·00	100·00...	100·00	100·00...	100·00	100·00...	100·00
Nitrogen	2·11...	3·01	0·23...	0·31	0·11...	0·57	1·28...	1·55
*Equivalent to soluble phosphates	20·57...	15·39	33·33...	36·02	19·10...	21·43	27·50...	19·77

Superphosphates made from bones alone are generally distinguished by a large quantity of ammonia, and rather a low percentage of biphosphate of lime. This is owing to the difficulty experienced in making the acid react in a satisfactory manner on bones, the phosphates being protected from its action by the large quantity of animal matter, which, when moistened, swells up, fills the pores, and prevents the ready access of the acid to the interior of the fragments. Super-

phosphates from bone ash, on the other hand, contain a mere trifle of ammonia, and when well made, a very large quantity of biphosphate of lime. Their quality differs very greatly, and depends, of course, on that of the bone ash employed, which can rarely be obtained of quality sufficient to yield more than 30 or 35 per cent. of soluble phosphates.

Coprolites are seldom used alone for the manufacture of superphosphates, but are generally mixed with bone ash and bone dust. Mixtures containing salts of ammonia, flesh, blood, etc., are also largely manufactured, and some are now produced containing as much as 4 or 5 per cent. of ammonia, and the consumption of such articles is largely increasing.

The following analyses (Anderson) illustrate the composition of some inferior varieties of superphosphates, in the manufacture of which the quantity of sulphuric acid has been reduced, and consequently containing a smaller proportion of soluble phosphates; these manures are sold in the market for much more than they are really worth:—

Water	21·60	5·37	7·19
Organic matter and ammoniacal salts	11·62	13·91	8·80
Biphosphate of lime	2·98	2·02	6·42
Insoluble phosphates	25·70	15·80	14·03
Sulphate of lime	23·60	47·52	51·93
Alkaline salts	10·70	3·73	3·43
Sand	3·80	11·65	8·20
	100·00	100.00	100·00
Ammonia	1·32	0·59	0·33

214. Bones.

The manurial value of bones is dependent partly on their phosphates, and partly on the nitrogen they yield. The following points should be attended to in estimating the value of of a sample:—

I. *Determination of Water.*—A weighed quantity is dried in the water-oven, until the weight remains constant.

II. *Determination of the total amount of fixed constituents.*—Introduce into a platinum crucible about 20 grains of the bone in a coarse powder; place the crucible in an oblique position over the gas or spirit burner, and allow it to remain until the ash has become quite white; the burning bone should be

turned over from time to time with a platinum wire; when cold, weigh the residue.

III. *Determination of the amount of Sand.*—Digest about 20 grains (or the residue of II.) with dilute hydrochloric acid; throw on a filter; wash, dry, ignite, and weigh the residue.

IV. *Determination of the Lime and Phosphoric Acid.*—To the filtrate from the sand (III.) add a few drops of ammonia, so as nearly to neutralize the liquor, then add oxalate of ammonia, boil, and then excess of acetate of ammonia; allow the precipitated oxalate of lime to subside, then filter it off, convert it into sulphate, and weigh. To the filtrate from the oxalate of lime, add tartaric acid, and then ammonio-sulphate of magnesia, and well agitate; filter off, after standing for a day; wash the precipitate on the filter with ammoniacal water, dry, ignite, and weigh as pyrophosphate of magnesia. This method recommends itself by its extreme simplicity, though it is not absolutely accurate, as it takes no cognizance of the *magnesia*, which all bones contain; as, however, it exhibits the total quantity of phosphoric acid (the real fertilizing agent), it gives all the information required for estimating the manurial value of the sample.

V. *Determination of the Nitrogen.*—Ignite from 15 to 20 grains with soda lime, precisely according to the method recommended for the analysis of ammoniacal salts. The result of the analysis will show the exact quantity of ammonia which the gelatine of the bone is capable of yielding by its decomposition.

VI. *Determination of the amount of Carbonic Acid, in combination with Lime, and perhaps Magnesia.*—This is effected by the method of Fresenius and Will.

In estimating the value of a manure, the particular element required by the soil to which it is intended to apply it, must be taken into account. "Thus" (observes Anderson), "a farmer who finds that his soil wants *phosphates*, will look to the manure containing the largest quantity of that substance, and possibly not requiring *ammonia*, will not care to estimate at its full value any quantity of that substance which he may be compelled to take along with the former; but will look only to the source from which he can obtain it most cheaply. It may be as well, therefore, to point out that *ammonia* is most cheaply purchased in Peruvian guano; *insoluble phosphates* in coprolites; and *soluble phosphates* in superphosphates made from bone-ash alone."

The bones used in agriculture are chiefly those of cattle. The following composition of the bones of the cow represents very nearly that of a *genuine* sample:—

Organic matter (gelatine)	33·25
Phosphate of lime	55·50
Phosphate of magnesia	3·00
Carbonate of lime	3·75
Soda and common salt	3·50
Chloride of calcium	1·00
	100·00

But bones are met with in commerce in other forms, in which their organic matter has been extracted, either by boiling or by burning; the latter is very common in the form of the spent animal charcoal of the sugar refiners, which usually contains from 70 to 80 per cent of phosphate of lime. It was formerly considered that the efficacy of bones as a manure depends solely on the quantity of phosphate which they contain, but the benefit derived from the nitrogenous constituent, which in the soil eventually takes the form of ammonia, is now fully recognized. The gelatine or organic part of bones consists of—

Carbon	50·37
Hydrogen	6·33
Nitrogen	17·95
Oxygen	25·35
	100·00

So that, supposing this animal substance to be decomposed in the soil, the quantity of it in 100lbs. of dry bone is sufficient to produce upwards of 6½ lbs. of ammonia, as much as is present in 20 lbs. of sal-ammoniac, or in 30 lbs. of crystallized sulphate of ammonia. Liebig has indeed advanced the opinion that the ammonia of the atmosphere will give nitrogen enough to the plant, provided the soil be sufficiently supplied with the *mineral matters* which it requires, but it is well known that the exhausted stiffening-liquor for calicoes, which, in Manchester, is largely made from bones by boiling them under pressure, has been applied as a liquid manure to grass lands, with the greatest success. Some years ago, at the suggestion of the late Professor Johnston, a series of experiments was made in Scotland to test the relative value of burnt and unburnt bones, and the general results were these:—

1st. That *whole* bones under favourable conditions seldom fail in raising an average crop of turnips.

2nd. That burnt bones in equivalent quantity do *not* always succeed in raising an average crop.

3rd. That when to the burnt bones, a sufficiency of organic matter in the form of farm-yard manure was added, then burnt bones produced the usual effects of whole bones. The farmer's surest reliance will therefore be on entire bones, especially if there be a deficiency of organic matter in his soil.

CHAPTER XII.

ON THE ANALYSIS OF THE ASHES OF VEGETABLE AND ANIMAL SUBSTANCES.

215. Analysis of Ashes of Vegetables.

(1.) *Method of Will and Fresenius* ('Memoirs and Proceedings of the Chemical Society,' vol. ii. p. 179):—

First preparation.—Plants in a normal and healthy condition should be selected, unless the design be to study diseases and their causes. All foreign matter, such as dirt, dust, etc., should be carefully removed; but the plants should not be washed, or certain soluble salts might be extracted. Plants which have been exposed to moist weather should, for the same reason, be rejected.

The design of analysing the ashes of plants may be—simply to ascertain the amount and nature of their inorganic constituents; or, the operator may have in view the discovery of the presence or absence of certain substances in the soil, such as *alkalies*, *alkaline earths*, and *phosphates*. For the latter purpose an examination of the ashes of all the varieties of plants growing upon the soil must be undertaken; and when a knowledge is hereby obtained of the composition of the inorganic constituents of both weeds and of cultivated plants, and when to this is added an acquaintance with the nature of the soluble constituents of the soil itself, the analyst is in a position to determine for what crops the soil in question is best adapted. *Woods*, *herbs*, and *roots*, after being perfectly dried, may be burnt upon a clean iron plate; *leaves*, *fruit*, and *seeds* may be burnt in a Hessian crucible, by means of charcoal or coke: the crucible should be placed somewhat obliquely in the fire, in order to favour the access of air. During the operation of burning, and especially towards the end of the process, the ashes should be allowed to lie as lightly in the crucible as

possible, in order that air might circulate freely through them; they should not, therefore, be stirred together: by attending to this, a much whiter ash is procured than would otherwise be the case. After the ashes have been well burnt in the crucible, it is advisable to transfer them to a platinum dish, and to heat them to low redness over a gas or spirit lamp, with constant stirring; they are generally left almost white, but some seeds require a higher temperature than others to rid the ashes entirely of charcoal: care must however be taken not to allow the heat to rise sufficiently high to fuse the alkaline salts, or it will be found afterwards almost impossible thoroughly to burn away the charcoal. The ash is rubbed to a fine powder, and transferred while warm to a well-stoppered bottle. Rose objects to this method of preparing ashes for analysis; his observations on this subject will be referred to further on.

The ash being prepared, the first step is to determine, by means of a qualitative examination, to which class the ashes belong,—whether to the *siliceous*, or to the *phosphoric*, or to the *carbonic* class. A small portion is treated with concentrated hydrochloric acid, which generally dissolves it completely, unless the ash abounds in silica; if a strong effervescence accompany the solution in hydrochloric acid, carbonates of the alkalies or alkaline earths predominate, and the whole of the phosphoric acid present is probably combined with peroxide of iron; if no (or only moderate) effervescence attend the solution, phosphates predominate; and if complete solution in hydrochloric acid cannot be obtained, the ash belongs to the siliceous class.

To the clear hydrochloric solution, acetate of ammonia is either at once added, or it is first neutralized by caustic ammonia, and free acetic acid afterwards added. In most cases a yellowish-white gelatinous precipitate is formed, consisting of *phosphate of peroxide of iron.* This precipitate is collected on a filter, and ammonia added in excess to the clear filtrate, by which means a fresh precipitate may be obtained; if it be red, it is peroxide of iron. The solution is well protected from the air, and allowed to stand for some time; if no further precipitation take place, then it is known that the ash contains no other phosphate than that previously precipitated; but should a white deposit gradually form, it consists of *phosphates of lime* and *magnesia*, and shows that the ash under examination contains more phosphoric acid than is combined with the peroxide of iron. It is not necessary to proceed further with the qualitative examina-

tion, unless the operator should wish to test for *fluorine*, *oxide of manganese*, *iodine*, *bromine*, or any other peculiar substance, the presence of which may be suspected, and in such cases separate portions of the ash must be used for each experiment, as also for determining quantitatively the amounts of carbonic acid in the ashes abounding in that principle, and of the alkalies in the ashes belonging to the *siliceous* class.

Determination of the quantity of Ashes yielded by a given weight of the Plant.—This is a problem, the solution of which is of considerable importance: a quantity of solid matter is annually removed from the soil in the crop taken from it, which loss should be repaired as nearly as possible by the judicious addition of manure. It is the nature of the manure to be furnished which the farmer seeks from the analytical chemist; but the farmer must take his share in the inquiry by informing the analyst as to the weight of the crop which a given surface of soil should yield, and this he can in most cases do with sufficient accuracy. The vegetable substance under examination should be dried in the water-bath, or still better in a current of dry air produced by the efflux of water in the apparatus, depicted in Fig. 65, page 252, till it ceases to lose weight. The quantity of substance employed in this experiment depends on the proportion of its inorganic constituents. Of *herbs* and *seeds*, which are in general rich in these matters, from 50 to 100 grains will be sufficient, whilst of *woods* ten times that amount must be taken. The combustion succeeds best in a muffle, the dried vegetable to be incinerated, being placed in a porcelain or platinum dish, which just fits into the muffle, which is gradually heated, the temperature not being allowed to rise beyond dull redness. Large cast-iron muffles, two or three of which may be heated by one fire, are exceedingly useful methods of applying heat in a laboratory. With the aid of a damper the temperature may be regulated with great accuracy, and kept uniform for any length of time. The time required to prepare an ash fit for analysis is from ten to twelve hours. In cases where a muffle is in the first place inadmissible, a large Hessian crucible may be used. It should at first be covered, and a gentle heat only applied, and the mass being carbonized should be reduced to ash in the muffle.

Those ashes which do not effervesce with acids, as the ashes of seeds, may be treated with nitric acid, and again ignited, by which treatment they will speedily be rendered quite white.

If a very strong heat has been employed, the carbonic acid, and in those ashes which effervesce with hydrochloric acid, will be expelled, but it may be restored by moistening the ashes with solution of carbonate of ammonia, and afterwards again exposing them to gentle ignition; so also, at a high temperature in contact with charcoal, the sulphates (if any be present) may be converted into sulphides, but the reconversion of those compounds into the original salts, may be effected by heating the ashes strongly, and for a considerable time, together with pure oxide of mercury. Although the above method of estimating the amount of ashes yielded by a plant is not altogether free from objection, it is, nevertheless, a sufficiently close approximation to truth to answer every practical purpose; indeed, it is doubtful whether more accurate methods would really be more valuable, since it is found that the amount of ashes yielded by the same plant is not constant.

Analysis of Ashes completely soluble in Hydrochloric Acid:—

Determination of the Silica, Charcoal, and Sand.—About 60 grains of the ashes, which have been found to be soluble in hydrochloric acid, are treated with concentrated acid in a flask held obliquely so as to avoid any loss of the liquid during the evolution of the carbonic acid; a gentle heat is then applied until it is evident that everything is dissolved excepting the carbonaceous and sandy particles. The whole is now carefully removed into a porcelain basin, evaporated to dryness over a water-bath, and then heated somewhat more strongly, as is usual in separating silica (see section 195). The mass when cold, is moistened with strong hydrochloric acid, digested for about half an hour with a sufficient quantity of water, and boiled, after which the acid liquor is poured upon a stout filter, which has previously been dried at 212°, and weighed. The silica remains on the filter, and if the ashes were not perfectly white and pure, some sand and charcoal also. The filter is washed and dried, and the substance carefully removed from it into a platinum or silver crucible without injury to the paper. This is effected without difficulty, if the matters be perfectly dry, the paper in most cases only retaining so much as to be slightly coloured by the charcoal. The powder is now boiled for half an hour with pure potassa-ley (free from silica); by which the whole of the silica, natural to the ash, will be gradually dissolved, leaving the sand and charcoal unacted upon. The insoluble matter is again collected on the same filter, and after being well washed, it is

dried at 212° till it no longer loses weight. The increase upon the weight of the dried filter is to be estimated as charcoal and sand. The silica in the alkaline solution is determined by adding hydrochloric acid in excess, whereby it is precipitated; the whole is evaporated to dryness, and the further treatment conducted in the usual manner.

The acid solution originally filtered from the *silica, sand*, and *charcoal*, after being well mixed, is divided into *three*, or more conveniently into *four* equal portions, one portion being reserved in case of an accident happening with either of the other quantities. The division is best effected by means of an accurately graduated tube or cylinder; the whole of the fluid is collected into the tube or cylinder, the measure of which thus represents the weight of ash experimented upon. The solution is now divided into three or four equal or known portions, the volume of each is noted, and they are labelled respectively with the letters *a*, *b*, *c*, and *d*.

In *a* the *peroxide of iron* (oxide of manganese) and the alkaline earths are estimated.

In *b* the alkalies.

In *c* the *sulphuric* and *phosphoric acids*.

(*a*.) *Estimation of the Phosphate of Peroxide of Iron, Peroxide of Iron, Oxide of Manganese, and Alkaline Earths.*—To the solution ammonia is added until the precipitate thereby produced no longer entirely redissolves; acetate of ammonia is next added, and sufficient acetic acid to render the solution strongly acid. From the form and appearance of the precipitate, it can easily be judged whether it contains *phosphate of lime;* if this be the case, more acetic acid must be added. The yellowish-white precipitate which remains consists of *phosphate of peroxide of iron* (Fe_2O_3, PO_5); its separation from the fluid is assisted by gently heating, it is then well washed on the filter with hot water, ignited, and weighed. To the filtered solution, neutral oxalate of ammonia is added as long as a precipitate continues to be formed, and the amount of lime is determined in the usual manner. When it has been shown by the qualitative analysis that, besides phosphate of iron, the ash contains peroxide of iron or oxide of manganese (in which case the presence of the earthy phosphates is very rarely detected), the solution, previous to the separation of the lime, should be supersaturated with ammonia, and precipitated by means of sulphide of ammonium, the two oxides being afterwards separated according

to one of the methods given in section 169. If the ashes under examination contained earthy phosphates, the solution filtered from the oxalate of lime will contain free acetic acid, if otherwise, there will be free ammonia; it is next somewhat concentrated, rendered ammoniacal, treated with a solution of phosphate of soda, and the precipitate formed, collected, and estimated as pyrophosphate of magnesia.

(*b.*) *Estimation of the Alkalies.*—The solution is treated with baryta water until it gives an alkaline reaction, it is then gently heated and filtered. By this means we get rid of all the *sulphuric* and *phosphoric acids*, the *peroxide of iron*, the *magnesia*, and part of the *lime*. The precipitate is washed on a filter as long as the washings render turbid a solution of nitrate of silver. It is next warmed, treated with caustic and carbonate of ammonia, and allowed to stand until the precipitate becomes heavy and granular. The whole is now filtered, and the solid matter washed, after which the solution is evaporated to dryness, and the residue heated to redness in a platinum capsule to expel the ammoniacal salts. What remains consists of the chlorides of potassium or sodium, or more generally of a mixture of the two. The weight being noted, a little water is added, which generally leaves undissolved a trace of magnesia; this is collected on a filter, its quantity subtracted from that of the supposed alkaline chlorides, and added to that of the magnesia, as previously ascertained. The quantity of potassa is determined by means of chloride of platinum in the usual way, and that of the soda is calculated from that of the chloride of sodium indicated by deducting the weight of the chloride of potassium from that of the mixed alkaline chlorides; or the amount of the two alkalies may be determined by the *indirect* method as directed in page 261.

(*c.*) *Estimation of the Sulphuric and Phosphoric Acids.*—Heat nearly to boiling, add chloride of barium in excess, allow the precipitated sulphate of baryta completely to subside, then filter it off, and after well washing, dry, ignite, and weigh.

If the ash effervesce strongly on the addition of hydrochloric acid, alkaline or earthy *carbonates* predominate, and the whole of the phosphoric acid is probably in the state of phosphate of iron. Should there be no effervescence, or an inconsiderable one, then phosphoric acid may exist in some other form of combination, and it will be found in the solution filtered off from the phosphate of iron (*a*), and the process must be modified

thus:—having removed the phosphate of iron precipitated by ammonia and acetic acid, boil with oxalate of ammonia, filter off the oxalate of lime, and divide the filtrate into two parts; in one determine the magnesia by the addition of ammonia and phosphate of soda, and in the other the phosphoric acid by the addition of ammonia, chloride of ammonium, and sulphate of magnesia.

Estimation of the Chlorine.—A fresh portion (about 15 grains) of the ashes is weighed out and exhausted with hot water, slightly acidulated with nitric acid; the solution is precipitated with nitrate of silver, following the directions given at page 351. If the ashes should contain appreciable quantities of *iodine* and *bromine*, these bodies will be found in the precipitated silver salt; for their quantitative estimation, however, a larger quantity of the ashes must be employed.

Estimation of the Carbonic Acid.—The amount of this acid is determined with the apparatus of Fresenius and Will (p. 268).

Analysis of Ashes abounding in Silica.—Ashes of this kind are in general only partially soluble in acids. Their alkalies must therefore be determined in a separate portion of the ash. The chlorine and carbonic acid are determined in the same manner as when the ash is entirely soluble in acids. The quantity of chlorine found in ashes of this class is, however, probably always somewhat less than it should be, since the alkaline chlorides, when ignited with silica and carbon, undergo a partial decomposition.

Estimation of the Silica.—Pure potassa or soda ley is poured upon about 60 grains of the ashes, and evaporated to dryness in a platinum or silver dish. The silicic acid compounds are, by this treatment, dissolved, leaving the sand unaffected. The heat should not be so great as to fuse the mass, or some of the charcoal might be oxidated at the expense of the water of the hydrated alkali. Diluted hydrochloric acid is poured upon the mass, the whole evaporated, and the silica, charcoal, etc., determined in the manner already described. The acidulous solution filtered from the insoluble matter is divided into two parts: one is employed for the determination of the sulphuric and phosphoric acids, and the other for that of the peroxide of iron and the alkaline earths by the methods detailed above.

Estimation of the Alkalies.—A second portion of the ash, (about 50 grains,) is ignited in a platinum crucible with four times its weight of *hydrate of baryta.* The acid solution which

remains after separating the silica, etc., is precipitated successively with baryta water and carbonate of ammonia, the alkalies being then obtained in the state of chlorides. The further treatment has already been described.

(2.) *Rose's method.*—It has been mentioned above that the method of preparing the ashes of plants for analysis by igniting the vegetable in Hessian crucibles, and continuing the heat until all organic matter is destroyed, has been objected to by Rose, who observes (Chem. Gaz., vol. v. p. 158) that, if the fixed constituents of plants are examined according to the process which he adopted in examining the ashes of *ox-blood*, results differing entirely from those yielded by the ash analyses hitherto published, may be obtained.

The process adopted by the Berlin chemist in his analyses of the ashes of blood was this. The blood was exposed in a covered platinum crucible to a very faint red-heat, then extracted with cold water, and the colourless liquid evaporated to dryness. It was found to consist of alkaline chlorides and carbonates, with very minute quantities of alkaline sulphates and phosphates. The charred mass, extracted with water, was now treated with hydrochloric acid: the filtered solution did not yield, with ammonia, a very considerable precipitate, which, though it looked almost like pure hydrated oxide of iron, contained some phosphoric acid as well as lime and magnesia. In the filtered solution a pretty considerable quantity of oxalate of lime was obtained with oxalate of ammonia, proving the presence of carbonate of lime in the charred blood; and in the liquid separated there was also a small quantity of magnesia. The cinder, after treatment with water and hydrochloric acid, yielded a very considerable quantity of a red-coloured ash, on being burnt in an atmosphere of oxygen. It was in a semifused state, and contained peroxide of iron (which formed the chief part) and earthy and alkaline phosphates.

These results differ considerably from those of M. Enderlin, whose method was (Liebig's 'Annalen' and Chem. Gaz., vol. iii. p. 229) to evaporate fresh blood to dryness, and then to powder and incinerate the residue. The ash thus obtained dissolved in hydrochloric acid *without* effervescence, whence he concluded that the alkalinity of blood cannot be caused by an alkaline carbonate, and that there cannot exist in the blood any alkaline salts with organic acids. The salts found by M. Enderlin in the ashes of blood he states to be *tribasic phosphate of soda*

($3NaO,PO_5$), *chlorides of sodium and potassium*, *sulphate of soda*, *phosphate of lime*, *phosphate of magnesia*, and *oxide*, with some *phosphate of iron*, the alkalinity of the blood being produced by phosphate of soda ($3NaO,PO_5$). If the phosphate of soda in the blood were the ordinary phosphate ($2NaO,HO,PO_5$), it would, according to M. Enderlin, be converted by a red heat into the *pyrophosphate* ($2NaO,PO_5$), the third atom of base (HO) escaping; but, according to Rose, the ordinary phosphate of soda ($2NaO,HO,PO_5$) would, at a high temperature, decompose *carbonate of soda* and be converted into tribasic phosphate ($3NaO,PO_5$); and that, in consequence, the conclusions of M. Enderlin are erroneous. It has been shown also by Marchand (Jour. für Prakt. Chem., April 6, 1846) that the circumstance of no carbonates being found in the ash, does not in the least prove that they are are not contained in the blood, and that we are as little justified in admitting unconditionally the presence of tribasic phosphate of soda ($3NaO,PO_5$) because that salt is found in the ash. Indeed Marchand declares that the admission of the presence of $3NaO,PO_5$ in the blood *absolutely requires* the admission of that of carbonate of soda, since it has been proved that $3NaO,PO_5$ is converted, on exposure to a moist atmosphere containing carbonic acid, into $2NaO,HO$ PO_5, and NaO,CO_2.

The same objections which have been urged against the conclusions drawn by Enderlin with regard to the salts existing in the blood, from the analysis of the ashes prepared at high temperatures, have been also applied by Rose to the conclusions drawn from the results of the analyses of the ashes of plants prepared in the usual manner. It had previously been remarked by Erdmann (Liebig's 'Annalen,' vol. lvi. and lvii.) that the mode of preparation of the ashes for analysis has great influence on their apparent composition. His method was to burn the plant or seeds in a muffle furnace, in which in the course of three or four hours, upwards of 200 grains of the most beautiful ash of corn may be obtained. The ashes so prepared, especially in those seeds that are difficult to reduce to ash, generally contain the phosphoric acid in a lower state of saturation than those prepared in a crucible. Thus the ash of rye, which usually contains an alkaline phosphate, yielding, with oxide of silver, a white precipitate, gives a yellow one when it has been prepared by long-continued ignition in a covered crucible; and biphosphate of potassa, when ignited for a long

time with carbonized sugar, is converted into a bibasic, and finally even into a tribasic salt. It is evident, therefore, that a reduction of the phosphoric acid has taken place, and the same is the case with the sulphuric acid. These facts induced Rose to undertake an examination of the fixed constituents of certain plants by the same method which he had adopted in the analysis of ox-blood, a method which, although it may be objected to in that it takes more time, furnishes (he says) far more correct results, and gives satisfactory answers to several questions as to how, or in what combinations, the constituents found in the ash were contained in the organic substance.

His method is as follows:—The organic substance is carbonized at a low red-heat in a capacious platinum or porcelain crucible, until a strong empyreumatic odour ceases to be perceived, and the carbonaceous mass yields no longer any yellow or brown substance to water. The remaining mass is now exhausted with hot water, as long as a few drops of the washings leave any considerable residue. The aqueous solution contains the alkaline salts (chlorides, sulphates, and phosphates) which existed *as such* in the organic substance, and frequently likewise alkaline carbonate which either pre-existed in the substance, or the alkali in it was combined with an organic acid, or some other organic body which acted the part of an acid towards the alkali; during the process of carbonization this organic acid was decomposed, carbonic acid being formed. The solution is evaporated nearly to dryness, diluted with water, allowed to stand for some time in order to separate the earthy salts (carbonates and phosphates of lime and magnesia) which had been dissolved in the salts of the alkalies; the precipitate is then filtered off, the filtrate dried up, weighed, and the acids and bases contained therein estimated by the usual methods.

The carbonized mass exhausted with water is now digested for some time with hydrochloric acid, and then washed with hot water, until a considerable quantity of the washings ceases to be precipitated by ammonia; the acid solution contains the earthy phosphates which were present as such, and sesquioxide of iron; these are precipitated by ammonia, and weighed together with the earthy salts deposited from the aqueous solution. The phosphoric acid in this precipitate is determined by nitric acid and metallic mercury in the manner described (p. 460). The liquid filtered from the earthy phosphates still contains some lime and magnesia, which are successively precipitated as oxalate and phosphate.

The carbonized mass exhausted by hydrochloric acid is yet rich in ash; it is by degrees completely incinerated in a thin porcelain crucible, through the perforated cover of which oxygen is passed, and the weight of the ashes added to that of the constituents extracted by water and hydrochloric acid. Subsequently Rose moistened the carbonaceous mass with bichloride of platinum before incinerating: the ash-grey residue thus obtained, is ignited in a stream of hydrogen gas, in order entirely to decompose the double salts of the alkaline chlorides with bichloride of platinum; then digested with hydrochloric acid, and the filtrate analysed in the same manner as the hydrochloric extract of the charcoal. The undissolved residue, consisting of platinum, sand, and silica, is either first boiled with carbonate of soda to remove the silica, and the platinum and sand then separated by *aqua-regia*, or the platinum is first extracted with *aqua-regia*, and the residue is then treated with carbonate of soda.

This method is exceedingly tedious and complicated; it has moreover been shown by Strecker (Ann. Ch. Pharm., lxxiii. 339), by Staffel (Ann. Pharm. (2) lxiv. 1, 129), and by Weber (Pogg. Ann., lxxxi. 402) that as regards chlorine it is incorrect, in consequence of which Rose (Pogg. Ann. lxxx. 9) modified his original proofs by mixing the charred organic substance with *spongy platinum*, incinerating it by small portions at a time in a platinum dish. The grey platiniferous mass obtained by incineration is heated in an air bath to 120° until its weight is constant. It is then treated with hot water, the aqueous solution evaporated to dryness, and the residue gently ignited and weighed. The dry residue is then divided into different portions and analysed in the usual manner. That part of the ash (containing platinum) which remains after extraction with water is treated with hot dilute nitric acid, and thoroughly washed with water acidulated with nitric acid. The solution contains phosphates of lime, magnesia, and sesquioxide of iron, together with nitrates of potassa, soda, lime, and magnesia, but no sulphuric acid or chlorine. It is treated with metallic mercury according to the method described (p. 460) for the determination of phosphoric acid, and the bases separated from the latter are determined in the ordinary way. The platinum residue is boiled with solution of caustic potassa which dissolves the silica; this is separated from the alkaline solution in the usual manner.

(3.) *Staffel's method* (Arch. der Pharm., lxiv. p. 1).—This is a modification of a method previously proposed by Wackenroder.

I. The organic substances are carbonized in a crucible, the lid of which is stuck on with starch paste. The lid has a hole through which the gases escape; these are inflamed. The charred mass is exhausted with water, and the aqueous extract (through which, if very alkaline, a stream of carbonic acid is passed) is evaporated to dryness and weighed. The solution of the weighed residue is acidified with nitric acid, and the silica being separated in the usual manner, the chloride is determined by nitrate of silver. The excess of silver being removed by hydrochloric acid, the solution is supersaturated with ammonia, and if no precipitate of phosphate of lime take place, the ammoniacal liquor is mixed with oxalic acid, for the separation of the lime. The liquid filtered from the oxalate of lime is precipitated with chloride of barium. The mixed oxalate, phosphate, and sulphate of baryta, after being dried and calcined, is digested with very dilute nitric acid, which leaves the sulphate of baryta undissolved. To the filtered liquid a slight excess of ammonia is added, and it is allowed to stand for some time. If any phosphate of baryta should be deposited, it is collected, dried, and calcined; and the phosphoric acid calculated according to the formula ($5BaO + 2PO_5$) containing 27·16 per cent. of phosphoric acid. There is still the potassa and soda to determine in the liquid filtered from the oxalate, sulphate, and phosphate of baryta. The excess of baryta is removed by carbonate of ammonia, and the alkalies are separated and estimated in the usual manner.

II. The charred and exhausted mass is reduced to ash in a Hessian crucible, placed in a slanting position. The ashes are weighed, and extracted repeatedly with water. The solution is divided into several parts: in one part, the chlorine is estimated; in another, (acidified with nitric acid) the silica; in a third the sulphuric and phosphoric acids are thrown down by chloride of barium, and separated as above described. The solution freed from the mixed barytic precipitates serves for the determination of the alkalies. In a fourth portion the lime and magnesia are estimated.

III. The residue, insoluble in water, is digested with hydrochloric acid. The solution is evaporated to dryness, and again dissolved in warm hydrochloric acid; the silica and sand in the insoluble residue are separated by caustic potassa. The hydro-

chloric solution is divided into two equal parts : in one, the alkalies are determined; the other serves for the estimation of the earths, peroxide of iron, and phosphoric acid, which is effected according to the following plan:—The solution is heated to boiling in a flask, mixed with acetate of soda and some acetic acid; the resulting precipitate, consisting of perphosphate of iron and phosphate of alumina, or of the first only, is collected on a filter, dried, calcined, and weighed. To separate the peroxide of iron from the alumina, the weighed precipitate is dissolved in hydrochloric acid, diluted with water, and heated to boiling for some time, with the addition of caustic potassa. The separated peroxide of iron is collected on a filter and calculated for phosphate of iron according to the formula (Fe_2O_3, PO_5) proposed by Wackenroder. The alumina is precipitated from the filtered alkaline liquid by acetic acid as phosphate of alumina (Al_2O_3, PO_5) dried, calcined, and weighed. In this case we must not omit to examine the mixed precipitate obtained by acetate of soda, for *phosphate of lime*, as frequently some is found in ashes which contain much phosphate of lime. If this precipitate be again dissolved in dilute hydrochloric acid, diluted with water, and heated to boiling with the addition of acetate of soda, it is obtained free from every trace of phosphate of lime. After the alumina and peroxide of iron have been precipitated by acetate of soda from the acid extract of the ash in the state of phosphate, the separated liquid is mixed with a solution of perchloride of iron (the amount of iron in which is known, and equal in weight to about the tenth or twentieth part of the entire weight of the ash), in order to determine the phosphoric acid still contained in it, the liquid itself is diluted with a considerable amount of water, heated to boiling in a flask with the addition of 6 or 7 grains of chlorate of potassa, nearly neutralized with carbonate of soda, and the whole of the iron added to the liquid thrown down as basic phosphate by the further addition of acetate of soda. The precipitate is collected on a filter, washed, dried, and ignited in a platinum dish after having been moistened with a few drops of nitric acid, and in this way a basic phosphate of iron is obtained perfectly free from protoxide. The liquid filtered from the basic phosphate of iron is heated to boiling in a flask with carbonate of soda, in order to precipitate lime, magnesia, and protoxide of manganese as carbonates. The filtered liquid is mixed with some phosphate of soda and ammonia, and the crystalline precipitate of ammonio-

phosphate of magnesia, obtained after twelve or twenty-four hours, added to that portion to be mentioned presently. The mixed precipitates of earthy carbonates are, after drying, heated to strong redness in a porcelain crucible, then dissolved in cold nitric acid. If any manganese be present it is left as Mn_3O_4. The separated liquid is mixed with oxalate of potassa, the oxalate of lime calcined after drying, and calculated from the amount of carbonate. After separating the oxalate of lime, the liquid is mixed with ammonio-phosphate of soda, and the crystalline precipitate obtained, after standing, is mixed with that previously obtained, calcined, and the weight of magnesia calculated from it. The other half of the liquid is examined for alkalies according to the usual method.

(4.) *Way and Ogston's method* ('Journal of the Royal Agricultural Society of England,' vols. viii. and ix.) :—

I. *Estimation of the Water in the vegetable.*—Grains are dried entire; bulbs, leaves, etc., are cut into small pieces; the temperature employed is at first about 150° or 160° F., at which it is kept for a fortnight; the vegetable is then weighed, and dried again for another week or fortnight; the drying is completed in the water oven at 212°, till there is no longer a loss of weight.

II. *Estimation of the percentage of Ash.*—From 100 to 200 grains of seeds, and from 60 to 80 grains of dried bulbs, leaves, etc., are burnt in a small platinum dish (watch-glass shape) over the air-flame of gas, the burning being continued till the ash is quite white; with ashes that fuse but still contain little silica, the burning is stopped before fusion begins. The weighed ash is treated with dilute hydrochloric acid; the charcoal (which seldom amounts to $\frac{1}{10}$ of a grain) is collected, washed, dried, weighed, and deducted. In all specimens burnt for analysis, the estimation is checked by the larger quantity.

III. *Burning the Ash for analysis.*—From 4000 to 6000 grains of seeds carefully cleaned, and from 1000 to 2000 grains of dried bulbs, leaves, etc., are burnt in a large platinum dish, over a Black's furnace, supported in the opening at the top, by a solid iron ring; the temperature never exceeds dull redness; there is perfect access of air, the dish being 8 or 10 inches broad, and 1½ inch deep only. The ash is stirred, when necessary, with a thick platinum wire; the burning is discontinued as soon as the charcoal ceases to glow at a dull red-heat.

The ash is in every case examined, in case of any trace of foreign matter having been overlooked; it is then powdered, dried, and weighed.

IV. *Estimation of Chlorine and Sulphuric Acid.*—15 or 20 grains are heated with water, and a small quantity of nitric acid added; the solution is filtered, and precipitated with nitrate of silver for chlorine; the excess of silver being thrown down from the precipitated chloride of silver by hydrochloric acid, the sulphuric acid is precipitated from the filtrate by chloride of barium.

V. *Estimation of Carbonic Acid.*—This is effected in 15 or 20 grains of the ash by one of the well-known methods. (See Carbonic Acid.)

VI. *Estimation of the Silica.*—If the ash be siliceous, or contain much charcoal, 40 or 50 grains are mixed with exactly its own weight of finely powdered and pure nitrate of baryta; the mixture is thrown by a platinum knife, by small portions, into a large platinum crucible gently heated by a spirit or gas lamp; a gentle deflagration occurs without loss; the ash becomes quite white, and is easily decomposed by acids; it is treated with hydrochloric acid, evaporated to dryness, and the silica separated as usual; correction is made for the sulphate of baryta present; the silica is dissolved by boiling for half an hour with caustic potassa, filtered, and the loss of weight ascertained; the silica is again separated by an acid and evaporation.

VII. *Estimation of the Alkalies.*—A certain measure of the liquid is precipitated successively by caustic baryta, and carbonate of ammonia mixed with caustic ammonia; evaporated to dryness, and the residue ignited and weighed. It is redissolved in a little water, treated with chloride of platinum, and the liquid evaporated to dryness on the water-bath; alcohol (containing a little ether) is added, and the salt collected on a filter, washed with the same liquid, and dried at 212°.

VIII. *Estimation of Perphosphate of Iron, Lime, and Magnesia.*—The remainder of the liquid is precipitated with dilute sulphuric acid; the sulphate of baryta is collected and weighed; it always contains some sulphate of lime, which admits of calculation from the quantity of nitrate of baryta employed. One portion of the filtered liquid is nearly neutralized by ammonia, acetate of ammonia added, warmed, and the phosphate of iron collected; the lime is precipitated by oxalate of ammonia, and the magnesia by phosphate of soda and am-

monia; to the lime is added that present in the sulphate of baryta.

IX. *Estimation of the Phosphoric Acid.*—A known quantity of the solution is nearly neutralized with ammonia; acetate of ammonia is then added, and from the filtrate now containing free acetic acid, the lime is precipitated by oxalate of ammonia; the solution filtered from the oxalate of lime is divided into two parts; in one, the magnesia is precipitated by ammonia, phosphate of soda being added if necessary; in the other portion the phosphoric acid is determined by means of sulphate of magnesia, chloride of ammonium, and ammonia, in the usual manner.

In ashes which contain but little silica or charcoal, the same method is followed, omitting the deflagration with nitrate of baryta.

With respect to Rose's method of preparing and analysing ashes, the conclusions at which Way and Ogston arrived after a laborious series of experiments may be summed up thus. It is impossible to burn a siliceous vegetable at any available temperature without a loss of carbonic acid; and in the absence of silica, phosphates with less than three atoms of base will, to a greater or less extent, act upon the carbonates of the ash, and thus vitiate the results as far as this acid is concerned. The method proposed by Rose of treating the charred vegetable by water and estimating the alkaline carbonate in solution can but partly remove this defect, for it leaves the insoluble *earthy* carbonates quite undetermined. In fact, we know of no method of burning plants so as to obtain estimations of the carbonic acid of their ashes which shall be at all indicative of the organic acids present in the vegetable substance. But a knowledge of the proportion of carbonic acid for practical purposes is not required. In the ordinary method of burning, there is a liability to loss of *sulphuric acid*, wherever silica is present, and where silica is not present there is always a loss of sulphur *not* existing in the plants as sulphuric acid, which loss is very variable in different experiments, depending on a variety of circumstances over which the operator can exercise no distinct control. The presence of phosphates does not appear to have any action upon the sulphates of the ash, and therefore the sulphuric acid afforded by an ordinary burning of a non-siliceous plant must represent the *full* quantity of that acid actually existing in the plant. There seems, at present, no method of distinguishing the *sulphuric acid* of the plant

from its *sulphur*, but an exact estimation of the *total* sulphur is obtained by digesting the plant with strong nitric acid, till the substance of it has been broken down into one uniform pulp, when the free acid is neutralized with pure carbonate of soda, and the mixture evaporated and carefully burnt. The ash is then introduced into a deep flask, and treated very gradually with strong nitric acid till it becomes acid. It is important to employ strong nitric acid, and a deep rather than an open vessel; because without these precautions there is a very considerable liability to loss, sulphuretted hydrogen being evolved from the alkaline sulphides produced in the last stages of the burning. The sulphuric acid in the nitric solution is estimated as sulphate of baryta in the usual manner. The ordinary methods of burning give perfectly accurate results for *phosphoric acid* both in siliceous and in non-siliceous ashes, provided an intense heat be not employed, in which case it is just possible that phosphorus may be reduced and dissipated, though from the tenacity with which phosphoric acid retains its last equivalent of base, such a result even then is more than questionable. Phosphates containing *two* atoms of a fixed base, with one of water, are not capable of decomposing chlorides at a high temperature, but phosphates with only *one* equivalent of a fixed base, and one or more of water, *do* decompose alkaline chlorides when heated with them, the chlorine escaping as hydrochloric acid; but there is good reason for believing that in the burning of plants, this water is dissipated by the heat long before the mineral substances of the ash can have been brought in sufficient contact to enable them to act upon each other. Direct experiments proved that it was quite possible to obtain coincident results in regard to chlorine by careful burning, though when an unusually high temperature is employed a loss of greater or less extent occurs; but this loss does not seem to be increased by the presence in the ash of a large proportion of silica or of phosphates. With respect to the alkalies, as they could only be lost in the form of chlorides, the same observations which apply to chlorine apply to those ingredients as plant ashes also. It is, after all, a matter of temperature, and the authors think that the discrepancies in the results obtained by different ash-analysts may, no doubt, be referable in many cases to this cause. The burning of a plant for analysis is plainly a process requiring considerable care,—a process that should, in no instance, be hurried forward;

but the authors submit that, on the whole, they have demonstrated that (with the exception of sulphur, which is obtained by a separate process) their method of burning crops affords an ash really and correctly representing the mineral matter of the plants under investigation.

(5.) *Strecker's method.*—He first chars the substance at a very low red-heat in a muffle, until fumes are no longer given off; it is then well mixed with a saturated solution of pure hydrate of baryta; evaporated to dryness and ignited at a low red-heat. The baryta ash is digested with aqua-regia and evaporated to dryness; the sulphur is hereby converted into sulphuric acid, and the phosphorus into phosphoric acid: it is then digested with hydrochloric acid and filtered: *silica, sulphate of baryta, charcoal*, and sand remain on the filter; the filtrate contains all the *phosphoric acid*, together with excess of baryta, lime and magnesia: it is treated with ammonia until a precipitate begins to fall, which is redissolved with a few drops of hydrochloric acid. To the slightly acid solution a sufficient quantity of ammoniacal sulphate of magnesia and tartaric acid is added: no precipitate takes place, because the solution is acid; oxalate of ammonia, and abundance of acetate of soda are now added, by which the excess of baryta and lime are precipitated as oxalates, and are filtered off: the phosphoric acid remains in the form of ammonio-magnesian phosphate in the acetic solution, from which it is precipitated by ammonia, filtered, and estimated as usual.

Arrangement of the results of analysis.—Since the analysis of the ashes of a plant can convey no precise information as to the manner in which the several acids and bases found are actually combined in the living vegetable, the method recommended by Fresenius and Will, namely, that of enumerating the percentage weights of the acids and bases found, is probably the best which the present state of our knowledge admits of; but, whether this or any other method be adopted, it is highly desirable that there should be uniformity on the subject, for it is only thus that the results of different analyses can be compared together, and so applied to the solution of certain interesting questions in physiology and in agriculture. The chlorine found in the analysis is always calculated as chloride of sodium, or chloride of potassium should the quantity of sodium be insufficient, and the manganese as *manganoso-manganic oxide* (Mn_3O_4).

216. Analysis of Ashes of Blood and Flesh.

I. *Of Blood* (Verdeil's process, Ann. Ch. Pharm., lxix. p. 89).—The blood is first charred in a porcelain crucible till no more empyreumatic vapour is evolved; the porous coal is powdered and incinerated in a muffle, and lastly, the ash is heated with nitrate of ammonia, which is dissolved in water and added by degrees. The coal is thus entirely burnt, and the carbonates are converted into nitrates, by which means a complete separation is effected of the constituents soluble in water from those which are insoluble. The ash of blood thus prepared, when digested with water and filtered, yields a perfectly neutral solution, which contains alkaline phosphates, nitrates, and sulphates, as well as metallic chlorides and phosphate of magnesia, whilst phosphate of lime and sesquioxide of iron remain behind. From the aqueous solution all the chlorine and phosphoric acid are precipitated by nitrate of silver. The precipitate when treated with dilute nitric acid, leaves *chloride* of silver, dissolving the *phosphate;* from the filtrate, the silver is precipitated by chloride of potassium, and the phosphoric acid is thrown down as ammonio-magnesian phosphate. From the solution which contains the alkalies, the sulphuric acid is removed by chloride of barium, the baryta and lime then precipitated by carbonate of ammonia and ammonia, the filtrate evaporated, and the residue ignited. On treatment with water the magnesia is left, whilst the alkalies are dissolved, and are determined as usual. The sesquioxide of iron, the lime, and the phosphoric acid are also determined by the usual methods in the portion which is insoluble in water. For the determination of the lime, the sulphuric and carbonic acids, separate quantities of ash are employed.

II. *Of Flesh, and Animal Substances generally* (Keller, Ann. Chem. Pharm., lxx. 91).—The animal matter is boiled repeatedly with water, and the solution separated from the residue by pressure. The liquid is evaporated, and the residue charred in a porcelain capsule; the powdered coal is boiled with water, and the undissolved residue is completely incinerated in the muffle. The residue of the flesh which has been boiled out and pressed is likewise dried and carbonized, and the coal, in a finely divided state, is treated for several days with strong nitric acid, after which it burns in the muffle very easily. The nitric solution is evaporated, and the ignited re-

sidue repeatedly heated with nitrate of ammonia, till all the coal has disappeared. The ashes thus obtained are intimately mixed, and ignited with three or four times their volume of fused hydrate of baryta. From the aqueous solution of the ignited mass, the baryta is removed by sulphuric acid or carbonate of ammonia, and the alkalies estimated in the filtrate. The portion insoluble in water, which contains all the phosphoric acid, is dissolved in the least possible quantity of nitric acid: the sulphate of baryta which separates, is weighed, and the phosphate of sesquioxide of iron precipitated by acetate of ammonia: from the acetic solution, the total amount of phosphoric acid is separated by acetate of lead. After the decomposition of the washed phosphate of lead by sulphate of ammonium, the phosphoric acid is precipitated from the filtrate by sulphate of magnesia. In the solution filtered from the phosphate of lead, the baryta and oxide of lead are precipitated by sulphuric acid, the filtrate (from which the last traces of lead are precipitated by sulphuretted hydrogen) is evaporated, and the lime and magnesia estimated as usual.

APPENDIX.

Table I.—*For the Calculation of Analyses.*

In the following Table the numbers have been re-calculated on the equivalent numbers assigned to the elementary substances in the Table, page 255, which is from the latest authorities.

The application of this Table, and its convenience in quantitative analysis, may be illustrated by the following example:—

Suppose as the result of an experiment to determine the amount of *sulphur* in a certain substance, 13·75 grains of sulphate of baryta have been obtained. On turning to the Table we find under the head of "required *sulphur*" found, "*sulphate of baryta*," a series of figures arranged in nine columns, those in the first column indicating the amount of sulphur in a *unit* of sulphate of baryta, and those in the other columns the multiples of that number by 2, 3, 4, 5, 6, 7, and 9. In the case we are considering, we require to learn the amount of sulphur in 13·75 grains of sulphate of baryta: we turn to Column 1, where we find the number 0·13734; we put down this number, shifting the decimal point one figure further to the *right;* we next turn to Column 3, where we find the number 0·41202; we place this number under the former, preserving the decimal point unaltered; the next number is 7, under which column we find the number 0·96138; we place this number under the last, shifting the decimal point one figure further to the *left;* in like manner the last number being 4, we write down the number found under that column, viz. 0·6870, shifting the decimal point two figures further to the left: the whole will consequently stand thus:—

$$\begin{array}{r} 1·373400 \\ 0·412020 \\ 0·096138 \\ \underline{0·006867} \\ 1·888425 \end{array}$$

13·75 grains of sulphate of baryta contain, therefore, 1·888 grains of sulphur.

TABLE I.

Required.	Found.	1	2	3	4	5	6	7	8	9
Aluminum Al_2	Alumina Al_2O_3	0·53390	1·06780	1·60170	2·13560	2·66950	3·20340	3·73730	4·27120	4·80510
Ammonia NH_3	Chloride of Ammonium NH_4Cl	0·31176	0·63552	0·95328	1·27104	1·58880	1·90656	2·22432	2·54208	2·85984
Ammonia NH_3	Ammonio-Chloride of Platinum $NH_4Cl, PtCl_2$	0·07623	0·15246	0·22869	0·30492	0·38115	0·45738	0·53361	0·60984	0·68607
Antimony Sb	Oxide of Antimony SbO_3	0·83561	1·67122	2·50683	3·34244	4·17805	5·01366	5·84927	6·38488	7·52049
Oxide of Antimony SbO_3	Sulphide of Antimony SbS_3	0·85881	1·71762	2·57643	3·43524	4·29405	5·15286	6·01167	6·87048	7·72929
Arsenic As	Arsenious Acid AsO_3	0·75757	1·51514	2·27271	3·03028	3·78785	4·54542	5·30299	6·06056	6·81813
Arsenic As	Arsenic Acid AsO_5	0·65217	1·30434	1·95651	2·60863	3·26085	3·91302	4·56519	5·21736	5·86958
Arsenious Acid AsO_3	Sulpharsenious Acid AsS_3	0·80488	1·60976	2·41464	3·21952	4·02440	4·82928	5·63416	6·43904	7·24392
Baryta BaO	Sulphate of Baryta BaO,SO_3	0·65665	1·31330	1·96995	2·62660	3·28325	3·93930	4·59655	5·25320	5·90985
Baryta BaO	Silico-fluoride of Barium $BaFl, SiFl_2$	0·54835	1·09670	1·64505	2·19340	2·74175	3·29010	3·83845	4·38680	4·93516
Bismuth Bi	Oxide of Bismuth BiO_3	0·89741	1·79482	2·69223	3·58964	4·48706	5·38447	6·28188	7·17929	7·97670
Boron B	Boracic Acid BO_3	0·31232	0·62464	0·93696	1·24928	1·56160	1·87392	2·18624	2·49856	2·81088

TABLE I. (*continued.*)

Required.	Found.	1	2	3	4	5	6	7	8	9
Bromine Br	Bromide of Silver $AgBr$	0·42554	0·85108	1·27662	1·70216	2·12770	2·55324	2·97878	3·40432	2·82986
Cadmium CdO	Oxide of Cadmium CdO	0·87500	1·75000	2·62500	3·50000	4·37500	5·25000	6·12500	7·00000	7·87950
Calcium Ca	Lime CaO	0·71429	1·42858	2·14287	2·85716	3·57145	4·28574	5·00013	5·71432	6·42861
Lime CaO	Sulphate of Lime CaO,SO_3	0·41176	0·82353	1·23529	1·64706	2·05881	2·47059	2·88233	3·29413	3·70585
Lime CaO	Carbonate of Lime CaO,CO_2	0·56000	1·12000	1·68000	2·24000	2·80000	3·36000	3·92000	4·48000	5·04000
Carbon C	Carbonic Acid CO_2	0·27273	0·54546	0·81819	1·09091	1·36365	1·63637	1·90912	2·18184	2·45457
Carbonic Acid CO_2	Carbonate of Lime CaO,CO_2	0·44000	0·88000	1·32000	1·76000	2·20000	2·64000	3·08000	3·52000	2·96000
Chlorine Cl	Chloride of Silver $AgCl$	0·24738	0·49476	0·74214	0·98952	1·23690	1·48428	1·73166	1·97904	2·22642
Hydrochloric Acid HCl	Chloride of Silver $AgCl$	0·25435	0·50870	0·76306	1·10740	1·27176	1·52612	1·78045	2·03480	2·28915
Chromium Cr_2	Oxide of Chromium Cr_2O_3	0·68643	1·37286	2·05929	2·74572	3·43215	4·11858	4·80501	5·49144	6·17787
Chromic Acid $2CrO_3$	Oxide of Chromium Cr_2O_3	1·31355	2·62710	3·94065	5·25420	6·56775	7·88130	9·19485	10·50840	11·82195
Chromic Acid CrO_3	Chromate of Lead PbO,CrO_3	0·31078	0·62156	0·93234	1·24312	1·55390	1·86468	2·17546	2·48624	2·79702
Protoxide of Cobalt CoO	Cobalt Co	1·27119	2·54238	3·81357	5·08476	6·35595	7·62714	8·89833	10·16952	11·44071

TABLE I. (*continued.*)

Required.	Found.	1	2	3	4	5	6	7	8	9
Copper Cu	Oxide of Copper CuO	0·79874	1·59748	2·39622	3·19496	3·99370	4·79244	5·59118	6·38992	7·18866
Fluorine F	Fluoride of Calcium CaF	0·48718	0·97436	1·46154	1·94872	2·43590	2·92308	3·41026	3·89744	4·38462
Hydrogen H	Water HO	0·11111	0·22222	0·33333	0·44444	0·55555	0·66667	0·77778	0·88889	1·00000
Iodine I	Iodide of Silver AgI	0·54043	1·08086	1·62129	2·16172	2·70215	3·24258	3·78301	4·32344	4·86387
Iron Fe_2	Sesquioxide of Iron Fe_2O_3	0·70000	1·40000	2·10000	2·80000	3·80000	4·20000	4·90000	5·60000	6·30000
Protoxide of Iron $2FeO$	Sesquioxide of Iron Fe_2O_3	0·90000	1·80000	2·70000	3·60000	4·50000	6·30000	6·30000	7·20000	8·10000
Lead Pb	Oxide of Lead PbO	0·92825	1·85650	2·78475	3·71300	4·64125	5·56950	6·49775	7·42600	8·35425
Oxide of Lead PbO	Sulphate of Lead PbO,SO_3	0·73597	1·47194	2·20791	2·94388	3·67785	4·41582	5·15179	5·88776	6·62373
Oxide of Lead PbO	Sulphide of Lead PbS	0·93306	1·86612	2·79918	3·73224	4·66530	5·59836	6·53142	7·46448	8·39754
Magnesia MgO	Sulphate of Magnesia MgO,SO_3	0·33510	0·67020	1·00530	1·34040	1·67550	2·01060	2·04570	2·68080	3·01590
Magnesia $2MgO$	Pyrophosphate of Magnesia $2MgO,PO_5$	0·36220	0·72440	1·08660	1·44880	1·81150	2·17320	2·53540	2·89760	3·25980
Manganese Mn_3	Protosesquioxide of Manganese Mn_3O_4	0·72052	1·44104	2·16156	2·88208	3·60260	4·32312	5·04364	5·76416	6·48468

TABLE I. (*continued.*)

Required.	Found.	1	2	3	4	5	6	7	8	9
Protoxide of Manganese MnO	Sulphate of Manganese MnO,SO_3	0·47020	9·40400	1·41060	1·88080	2·35100	2·82120	3·29140	3·76160	4·23180
Mercury Hg_2	Subchloride of Mercury Hg_2Cl	0·84925	1·69850	2·54775	3·39700	4·24625	5·09550	5·94475	6·79400	7·64325
Mercury Hg	Sulphide of Mercury HgS	0·86207	1·72414	2·58261	3·44828	4·31035	5·17242	6·03449	6·89656	7·75863
Nickel Ni	Oxide of Nickel NiO	0·78666	1·57332	2·35998	3·14664	3·93330	4·71996	5·50662	6·29328	7·07994
Nitrogen N	Ammonio-chloride of Platinum $NH_4Cl,PtCl$	0·06278	0·12556	0·18834	0·25112	0·31390	0·37668	0·43936	0·50224	0·56502
Nitrogen N	Platinum Pt	0·14213	0·28426	0·42639	0·56852	0·71065	0·85278	0·99491	1·13704	1·27917
Nitric Acid NO_5	Sulphate of Baryta BaO,SO_3	0·46352	0·92704	1·39056	1·83408	2·31760	2·78112	3·24464	3·60816	4·17168
Cyanogen C_2N	Cyanide of Silver AgC_2N	0·19403	0·38806	0·58209	0·77612	0·97015	1·16418	1·35821	1·55224	1·74627
Hydrocyanic Acid HC_2N	Cyanide of Silver AgC_2N	0·20149	0·40298	0·60447	0·80596	1·00745	1·20894	1·41043	1·61192	1·81331
Phosphorus P	Phosphoric Acid PO_5	0·43662	0·87324	1·30986	1·74648	2·18309	2·61972	3·05664	3·49296	3·92958
Phosphoric Acid PO_5	Pyrophosphate of Magnesia $2MgO,PO_5$	0·63780	1·27560	1·91340	2·55120	3·18900	3·82680	4·46460	5·10240	5·74020
Phosphoric Acid PO_5	Phosphate of Sesquioxide of Iron Fe_2O_3,PO_5	0·47020	0·94040	1·41060	1·88080	2·35100	2·82120	3·29140	3·76160	4·23180

TABLE I. (*continued.*)

Required.	Found.	1	2	3	4	5	6	7	8	9
Phosphoric Acid PO_5	Phosphate of Silver $3AgO,PO$	0·16945	0·33891	0·50835	0·67782	0·84725	1·01670	1·18615	1·35564	1·52505
Potassa KO	Sulphate of Potassa KO,SO_3	0·54023	1·08046	1·62069	2·16092	2·70115	3·24138	3·78161	4·32184	4·86202
Potassa KO	Nitrate of Potassa KO,NO_5	0·46534	0·93068	1·39602	1·83136	2·32670	2·79204	3·25738	3·72272	4·18806
Potassium K	Chloride of Potassium KCl	0·52349	1·04699	1·57047	2·09396	2·61745	3·14094	3·66443	4·18792	4·71141
Potassa KO	Chloride of Potassium KCl	0·63087	1·26176	1·89261	2·52348	3·15435	3·78522	4·41609	5·04696	5·67783
Potassa KO	Potassio-Chloride of Platinum $KCl,PtCl_2$	0·19262	0·38524	0·57786	0·77048	0·96310	1·15572	1·34834	1·50496	1·73358
Chloride of Potassium KCl	Potassio-Chloride of Platinum $KCl,PtCl_2$	0·30533	0·61066	0·91599	1·22132	1·52665	1·82198	2·13731	2·44264	2·74797
Silicon Si	Silicic Acid SiO_2	0·46667	0·93334	1·40001	1·86668	2·33335	2·80002	3·26669	3·73336	4·20003
Silver Ag	Chloride of Silver $AgCl$	0·75261	1·50522	2·25783	3·01044	3·76305	4·51566	5·26827	6·02088	6·77349
Sodium Na	Soda NaO	0·74193	1·48386	2·22579	2 96772	3·70965	4·45158	5·19351	5·93544	6·67737
Soda NaO	Sulphate of Soda NaO,SO_3	0·43662	0·87324	1·30986	1·74648	2·18310	2·61972	3·05634	2·49296	3·92958
Soda NaO	Nitrate of Soda NaO,NO_5	0·36470	0·72940	1·09410	1·45880	1·82350	2·18820	2·55290	2·91760	3·28230

TABLE I.—(*continued.*)

Required.	Found.	1	2	3	4	5	6	7	8	9
Soda NaO	Chloride of Sodium $NaCl$	0·52991	1·05982	1·58973	2·11964	2·64955	3·17946	3·70937	4·23928	4·76919
Sodium Na	Chloride of Sodium $NaCl$	0·39316	0·78362	1·17948	1·52764	1·96580	2·35896	2·75212	3·14528	3·53844
Strontium Sr	Strontia SrO	0·84541	1·69082	2·53623	3·38164	4·22705	5·07246	5·91787	6·76328	7·60869
Strontia SrO	Carbonate of Strontia SrO,CO_2	0·70169	1·40338	2·10507	2·80676	3·50845	4·21014	4·91183	5·61352	6·31521
Sulphur S	Sulphate of Baryta BaO,SO_3	0·13734	0·27468	0·41202	0·54936	0·68670	0·82404	0·96138	1·09872	1·23606
Sulphur S_3	Tersulphide of Arsenic AsS_3	0·39024	0·78049	1·17073	1·56097	1·95122	2·34146	2·73170	3·12194	3·51219
Sulphuric Acid SO_3	Sulphate of Baryta BaO,SO_3	0·34335	0·68671	1·03006	1·37342	1·71675	2·06013	2·40345	2·74684	3·09015
Tin Sn	Oxide of Tin SnO_2	0·78667	1·57334	2·36001	3·14668	3·93335	4·72002	5·50669	6·29336	7·08003
Protoxide of Tin SnO	Binoxide of Tin SnO_2	0·89334	1·78668	2·68002	3·57336	4·46670	5·36004	6·25338	7·14672	8·04006
Zinc Zn	Oxide of Zinc ZnO	0·80369	1·60738	2·41107	3·21476	4·01845	4·82214	5·62583	6·42952	7·23321
Oxide of Zinc ZnO	Sulphate of Zinc ZnO,SO_3	0·50465	1·00930	1·51395	2·01880	2·52325	3·02790	3·53255	4·03720	4·54185

TABLE II.—*French Measures of Weight, with their English Equivalents.*

	In English grains.	In troy ounces = 480 grains.	In avoirdupois pounds = 7000 grains.	In cwts. = 112 lb. = 784000 grains.	Tons = 20 cwts. = 15680000 grs.
Milligramme ...	0·01543	0·000032	0·0000022	0·0000000	0·0000000
Centigramme ...	0·15432	0·000322	0·0000220	0·0000002	0·0000000
Décigramme ...	1·54323	0·003215	0·0002205	0·0000020	0·0000001
Gramme	15·43235	0·032151	0·0022046	0·0000197	0·0000010
Dékagramme ...	154·32349	0·321507	0·0220462	0·0001968	0·0000098
Hectogramme...	1543·23488	3·215073	0·2204621	0·0019684	0·0000984
Kilogramme ...	15432·34880	32·150727	2·2046213	0·0196841	0·0009842
Myriogramme...	154323·48800	321·507267	22·0462126	0·1968412	0·0098421

1 grain = 0·064799 gramme; 1 troy ounce = 31·103496 grammes; 1 lb. avoir. = 0·453595 kilogrs.; 1 cwt. = 50·802377 kilogrs.

TABLE III.—*French Measures of Length, with their English Equivalents.*

	In English inches.	In English feet.	In English yards.	In English miles.
Millimètre ...	0·03937	0·003281	0·0010936	0·0000006
Centimètre ...	0·39371	0·032809	0·0109363	0·0000062
Décimètre ...	3·93708	0·328090	0·1093633	0·0000621
Mètre	39·37079	3·280899	1·0936331	0·0006214
Dékamètre ...	393·70790	32·808992	10·9363310	0·0062138
Hectomètre...	3937·07900	328·089920	109·3633100	0·0621382
Kilomètre ...	39370·79000	3280·899200	1093·6331000	0·6213824
Myriomètre...	393707·90000	32808·992000	10936·3310000	6·2138244

1 inch = 2·539954 centimètres; 1 yard = 0·9143835 mètre.
1 foot = 3·0479449 décimètres; 1 mile = 1·6093149 kilomètre.

TABLE IV.—*French Measures of Surface, with their English Equivalents.*

	In English square feet.	In English square yards.	In English acres = 43560 square feet.
Centiare, or square mètre...	10·764299	1·196033	0·0002471
Are, or 100 square mètres	1076·429934	119·603326	0·0247114
Hectare, or 10,000 square mètres	107642·993418	11960·332602	2·4711431

1 square inch = 6·4513669 square centimètres; 1 square yard = 0·83609715 square mètres.
1 square foot = 9·2899683 square décimètres; 1 acre = 0·40467102 hectare.

TABLE V.—*French Measures of Capacity with their English Equivalents.*

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints = 34·65923 cubic inches.	In gallons = 8 pints = 277·27384 cubic inches.	In bushels = 8 gallons = 2218·19075 cubic inches.
Millilitre, or cubic centimètre	0·06103	0·000035	0·00176	0·0002201	0·0000275
Centilitre, or 10 cubic centimètres	0·61027	0·000353	0·01761	0·0022010	0·0002751
Décilitre, or 100 cubic centimètres.........	6·10271	0·003532	0·17608	0·0220097	0·0027512
Litre, or cubic décimètre	61·20705	0·035317	1·76077	0·2200967	0·02751208
Dékalitre, or centistère.........................	610·27052	0·353166	17·60773	2·2009688	0·27512085
Hectolitre, or décistère	6102·70515	3·531658	176·07734	22·0096677	2·7512085
Kilolitre, or stère, or cubic mètre	61027·05152	35·316581	1760·77341	220·0966767	27·5120846
Myriolitre, or décastère	610270·51519	353·165807	17607·73414	2200·9667675	275·1208459

1 cubic inch = 16·386176 cubic centimètres; 1 cubic foot = 28·315312 cubic décimètres; 1 gallon = 4·543358 litres; a litre of water weighs a kilogramme; a cubic centimètre of water weighs a gramme.

Table VI.—*For the Comparison of the Centigrade and Fahrenheit Thermometers.*

$$n^\circ C = \frac{9}{5} n^\circ + 32^\circ F. \qquad n^\circ F = \frac{5}{9}(n^\circ - 32^\circ) C.$$

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
−50°	−58°·0	−5°	23°·0	40°	104°·0	85°	185°·0
−49	−56·2	−4	24·8	41	105·8	86	186·8
−48	−54·4	−3	26·6	42	107·6	87	188·6
−47	−52·6	−2	28·4	43	109·4	88	190·4
−46	−50·8	−1	30·2	44	111·2	89	192·2
−45	−49·0	0	32·0	45	113·0	90	194·0
−44	−47·2	+1	33·8	46	114·8	91	195·8
−43	−45·4	2	35·6	47	116·6	92	197·6
−42	−43·6	3	37·4	48	118·4	93	199·4
−41	−41·8	4	39·2	49	120·2	94	201·2
−40	−40·0	5	41·0	50	122·0	95	203·0
−39	−38·2	6	42·8	51	123·8	96	204·8
−38	−36·4	7	44·6	52	125·6	97	206·6
−37	−34·6	8	46·4	53	127·4	98	208·4
−36	−32·8	9	48·2	54	129·2	99	210·2
−35	−31·0	10	50·0	55	131·0	100	212·0
−34	−29·2	11	51·8	56	132·8	101	213·8
−33	−27·4	12	53·6	57	134·6	102	215·6
−32	−25·6	13	55·4	58	136·4	103	217·4
−31	−23·8	14	57·2	59	138·2	104	219·2
−30	−22·0	15	59·0	60	140·0	105	221·0
−29	−20·2	16	60·8	61	141·8	106	222·8
−28	−18·4	17	62·6	62	143·6	107	224·6
−27	−16·6	18	64·4	63	145·4	108	226·4
−26	−14·8	19	66·2	64	147·2	109	228·2
−25	−13·0	20	68·0	65	149·0	110	230·0
−24	−11·2	21	69·8	66	150·8	111	231·8
−23	− 9·4	22	71·6	67	152·6	112	233·6
−22	− 7·6	23	73·4	68	154·4	113	235·4
−21	− 5·8	24	75·2	69	156·2	114	237·2
−20	− 4·0	25	77·0	70	158·0	115	239·0
−19	− 2·2	26	78·8	71	159·8	116	240·8
−18	− 0·4	27	80·6	72	161·6	117	242·6
−17	+ 1·4	28	82·4	73	163·4	118	244·4
−16	3·2	29	84·2	74	165·2	119	246·2
−15	5·0	30	86·0	75	167·0	120	248·0
−14	6·8	31	87·8	76	168·8	121	249·8
−13	8·6	32	89·6	77	170·6	122	251·6
−12	10·4	33	91·4	78	172·4	123	253·4
−11	12·2	34	93·2	79	174·2	124	255·2
−10	14·0	35	95·0	80	176·0	125	257·0
− 9	15·8	36	96·8	81	177·8	126	258·8
− 8	17·6	37	98·6	82	179·6	127	260·6
− 7	19·4	38	100·4	83	181·4	128	262·4
− 6	21·2	39	102·2	84	183·2	129	264·2

TABLE VI.—(*continued.*)

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
130°	266·0°	179°	354·2°	228°	442·4°	277°	530·6°
131	267·8	180	356·0	229	444·2	278	532·4
132	269·6	181	357·8	230	446·0	279	534·2
133	271·4	182	359·6	231	447·8	280	536·0
134	273·2	183	361·4	232	449·6	281	537·8
135	275·0	184	363·2	233	451·4	282	539·6
136	276·8	185	365·0	234	453·2	283	541·4
137	278·6	186	366·8	235	455·0	284	543·2
138	280·4	187	368·6	236	456·8	285	545·0
139	282·2	188	370·4	237	458·6	286	546·8
140	284·0	189	372·2	238	460·4	287	548·6
141	285·8	190	374·0	239	462·2	288	550·4
142	287·6	191	375·8	240	464·0	289	552·2
143	289·4	192	377·6	241	465·8	290	554·0
144	291·2	193	379·4	242	467·6	291	555·8
145	293·0	194	381·2	243	469·4	292	557·6
146	294·8	195	383·0	244	471·2	293	559·4
147	296·6	196	384·8	245	473·0	294	561·2
148	298·4	197	386·6	246	474·8	295	563·0
149	300·2	198	888·4	247	476·6	296	564·8
150	302·0	199	390·2	248	478·4	297	566·6
151	303·8	200	892·0	249	480·2	298	568·4
152	305·6	201	393·8	250	482·0	299	570·2
153	307·4	202	395·6	251	483·8	300	572·0
154	309·2	203	397·4	252	485·6	301	573·8
155	311·0	204	399·2	253	487·4	302	575·6
156	312·8	205	401·0	254	489·2	303	577·4
157	314·6	206	402·8	255	491·0	304	579·2
158	316·4	207	404·6	256	492·8	305	581·0
159	318·2	208	406·4	257	494·6	306	582·8
160	320·0	209	408·2	258	496·4	307	584·6
161	321·8	210	410·0	259	498·2	308	586·4
162	323·6	211	411·8	260	500·0	309	588·2
163	325·4	212	413·6	261	501·8	310	590·0
164	327·2	213	415·4	262	503·6	811	591·8
165	329·0	214	417·2	263	505·4	312	593·6
166	330·8	215	419·0	264	507·2	313	595·4
167	332·6	216	420·8	265	509·0	314	597·2
168	334·4	217	422·6	266	510·8	315	599·0
169	336·2	218	424·4	267	512·6	316	600·8
170	338·0	219	426·2	268	514·4	817	602·6
171	339·8	220	428·0	269	516·2	318	604·4
172	341·6	221	429·8	270	518·0	319	606·2
173	343·4	222	431·6	271	519·8	320	608·0
174	345·2	223	433·4	272	521·6		
175	347·0	224	435·2	273	523·4		
176	348·8	225	437·0	274	525·2		
177	350·6	226	438·8	275	527·0		
178	352·4	227	440·6	276	528·8		

TABLE VII.—*Showing the Quantity of Oil of Vitriol of Specific Gravity* 1·8485, *and of Anhydrous Acid, in* 100 *Parts of dilute Sulphuric Acid, of different Densities, according to Dr. Ure.*

Liquid.	Specific Gravity.	Dry.	Liquid.	Specific Gravity.	Dry.
100	1·8485	81·54	50	1·3884	40·77
99	1·8475	80·72	49	1·3788	39·95
98	1·8460	79·90	48	1·3697	39·14
97	1·8439	79·09	47	1·3612	38·32
96	1·8410	78·28	46	1·3530	37·51
95	1·8376	77·46	45	1·3440	36·69
94	1·8336	76·65	44	1·3345	35·88
93	1·8290	75·83	43	1·3255	35·06
92	1·8233	75·02	42	1·3165	34·25
91	1·8179	74·20	41	1·3080	33·43
90	1·8115	73·39	40	1·2999	32·61
89	1·8043	72·57	39	1·2913	31·80
88	1·7962	71·75	38	1·2826	30·98
87	1·7870	70·94	37	1·2740	30·17
86	1·7774	70·12	36	1·2654	29·35
85	1·7673	69·31	35	1·2572	28·54
84	1·7570	68·49	34	1·2490	27·72
83	1·7465	67·68	33	1·2409	26·91
82	1·7360	66·86	32	1·2334	26·09
81	1·7245	66·05	31	1·2260	25·28
80	1·7100	65·23	30	1·2184	24·46
79	1·6993	64·42	29	1·2108	23·65
78	1·6870	63·60	28	1·2032	22·83
77	1·6750	62·78	27	1·1956	22·01
76	1·6630	61·97	26	1·1876	21·20
75	1·6520	61·15	25	1·1792	20·38
74	1·6415	60·34	24	1·1706	19·57
73	1·6321	59·52	23	1·1626	18·75
72	1·6204	58·71	22	1·1549	17·94
71	1·6090	57·89	21	1·1480	17·12
70	1·5975	57·08	20	1·1410	16·31
69	1·5868	56·26	19	1·1330	15·49
68	1·5760	55·45	18	1·1246	14·68
67	1·5648	54·63	17	1·1165	13·86
66	1·5503	53·82	16	1·1090	13·05
65	1·5390	53·00	15	1·1019	12·23
64	1·5280	52·18	14	1·0953	11·41
63	1·5170	51·37	13	1·0887	10·60
62	1·5066	50·55	12	1·0809	9·78
61	1·4960	49·74	11	1·0743	8·97
60	1·4860	48·92	10	1·0682	8·15
59	1·4760	48·11	9	1·0614	7·34
58	1·4660	47·29	8	1·0544	6·52
57	1·4560	46·48	7	1·0477	5·71
56	1·4460	45·66	6	1·0405	4·89
55	1·4360	44·85	5	1·0336	4·08
54	1·4265	44·03	4	1·0268	3·26
53	1·4170	43·22	3	1·0206	2·446
52	1·4073	42·40	2	1·0140	1·63
51	1·3977	41·58	1	1·0974	0·8154

TABLE VIII.—*Showing the Quantity of Real or Anhydrous Nitric Acid in 100 Parts of Liquid Acid, at different Densities, according to Dr. Ure.*

Specific Gravity.	Real Acid in 100 Parts of the Liquid.	Specific Gravity.	Real Acid in 100 Parts of the Liquid.
1·5000	79·700	1·2947	39·850
1·4980	78·903	1·2887	39·053
1·4960	78·106	1·2826	38·256
1·4940	77·309	1·2765	37·459
1·4910	76·512	1·2705	36·662
1·4880	75·715	1·2644	35·865
1·4850	74·918	1·2583	35·068
1·4820	74·121	1·2523	34·271
1·4790	73·324	1·2462	33·474
1·4760	72·527	1·2402	32·677
1·4730	71·730	1·2341	31·880
1·4700	70·933	1·2277	31·083
1·4670	70·136	1·2212	30·286
1·4640	69·339	1·2148	29·489
1·4600	68·542	1·2084	28·692
1·4570	67·745	1·2019	27·895
1·4530	66·948	1·1958	27·098
1·4500	66·155	1·1895	26·301
1·4460	65·354	1·1833	25·504
1·4424	64·557	1·1770	24·707
1·4385	63·760	1·1709	23·900
1·4346	62·963	1·1648	23·113
1·4306	62·166	1·1587	22·316
1·4269	61·369	1·1526	21·519
1·4228	60·572	1·1465	20·722
1·4189	59·775	1·1403	19·925
1·4147	58·978	1·1345	19·128
1·4107	58·181	1·1286	18·331
1·4065	57·384	1·1227	17·534
1·4023	56·587	1·1168	16·737
1·3978	55·790	1·1109	15·940
1·3945	54·993	1·1051	15·143
1·3882	54·196	1·0993	14·346
1·3833	53·399	1·0935	13·549
1·3783	52·602	1·0878	12·752
1·3732	51·805	1·0821	11·955
1·3681	51·068	1·0764	11·158
1·3630	50·211	1·0708	10·361
1·3579	49·414	1·0651	9·564
1·3529	48·617	1·0595	8·767
1·3477	47·820	1·0540	7·970
1·3427	47·023	1·0485	7·173
1·3376	46·226	1·0430	6·376
1·3323	45·429	1·0375	5·579
1·3270	44·632	1·0320	4·782
1·3216	43·835	1·0267	3·985
1·3113	43·038	1·0212	3·188
1·3110	42·241	1·0159	2·391
1·3056	41·444	1·0106	1·594
1·3001	40·647	1·0053	0·797

TABLE IX.—*Showing the Quantity of Absolute Alcohol in Spirits of different Specific Gravities, according to Lowitz.*

100 Parts.		Specific Gravity.		100 Parts.		Specific Gravity.	
Alcohol.	Water.	At 68°.	At 60°.	Alcohol.	Water.	At 68°.	At 60°.
100	0	0·791	0·796	49	51	0·917	0·920
99	1	0·794	0·798	48	52	0·919	0·922
98	2	0·797	0·801	47	53	0·921	0·924
97	3	0·800	0·804	46	54	0·923	0·926
96	4	0·803	0·807	45	55	0·925	0·928
95	5	0·805	0·809	44	56	0·927	0·930
94	6	0·808	0·812	43	57	0·930	0·933
93	7	0·811	0·815	42	58	0·932	0·935
92	8	0·813	0.817	41	59	0·934	0·937
91	9	0·816	0·820	40	60	0·936	0·939
90	10	0·818	0·822	39	61	0·938	0·941
89	11	0·821	0·825	38	62	0·940	0·943
88	12	0·823	0·827	37	63	0·942	0·945
87	13	0·826	0·830	36	64	0·944	0·947
86	14	0·828	0·832	35	65	0·946	0·949
85	15	0·831	0·835	34	66	0·948	0·951
84	16	0·834	0·838	33	67	0·950	0·953
83	17	0·836	0·840	32	68	0·952	0·955
82	18	0·839	0·843	31	69	0·954	0·957
81	19	0·842	0·846	30	70	0·956	0·958
80	20	0·844	0·848	29	71	0·957	0·960
79	21	0·847	0·851	28	72	0·959	0·962
78	22	0·849	0·853	27	73	0·961	0·963
77	23	0·851	0·855	26	74	0·963	0·965
76	24	0·853	0·857	25	75	0·965	0·967
75	25	0·856	0·860	24	76	0·966	0·968
74	26	0·859	0·863	23	77	0·968	0·970
73	27	0·861	0·865	22	78	0·970	0·972
72	28	0·863	0·867	21	79	0·971	0·973
71	29	0·866	0·870	20	80	0·973	0·974
70	30	0·868	0·872	19	81	0·974	0·975
69	31	0·870	0·874	18	82	0·976	0·977
68	32	0·872	0·875	17	83	0·977	0·978
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66	34	0·877	0·881	15	85	0·980	0·981
65	35	0·880	0·883	14	86	0·981	0·982
64	36	0·882	0·886	13	87	0·983	0·984
63	37	0·885	0·889	12	88	0·985	0·986
62	38	0·887	0·891	11	89	0·986	0·987
61	39	0·889	0·893	10	90	0·987	0·988
60	40	0·892	0·896	9	91	0·988	0·989
59	41	0·894	0·898	8	92	0·989	0·990
58	42	0·896	0·900	7	93	0·991	0·991
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55	45	0·903	0·906	4	96	0·995	
54	46	0·905	0·908	3	97	0·997	
53	47	0·907	0·910	2	98	0·998	
52	48	0·909	0·912	1	99	0·999	
51	49	0·912	0·915	0	100	1·000	
50	50	0·914	0·917				

TABLE X.—*Showing the Quantity of Absolute Alcohol by Weight in Mixtures of Alcohol and Water of different Specific Gravities, according to Mr. Drinkwater.**

Sp. Gr. at 60° F.	Alcohol per cent. by weight.	Sp. Gr. at 60° F.	Alcohol per cent. by weight.	Sp. Gr. at 60° F.	Alcohol per cent. by weight.	Sp. Gr. at 60° F.	Alcohol per cent. by weight.
1·0000	0·00	·9959	2·22	·9918	4·64	·9877	7·30
·9999	0·05	·9958	2·28	·9917	4·70	·9876	7·37
·9998	0·11	·9957	2·34	·9916	4·76	·9875	7·43
·9997	0·16	·9956	2·37	·9915	4·82	·9874	7·50
·9996	0·21	·9955	2·45	·9914	4·88	·9873	7·57
·9995	0·26	·9954	2·51	·9913	4·94	·9872	7·64
·9994	0·32	·9953	2·57	·9912	5·01	·9871	7·71
·9993	0·37	·9952	2·62	·9911	5·07	·9870	7·68
·9992	0·42	·9951	2·68	·9910	5·13	·9869	7·85
·9991	0·47	·9950	2·74	·9909	5·20	·9868	7·92
·9990	0·53	·9949	2·79	·9908	5·26	·9867	7·99
.9989	0·58	·9948	2·85	·9907	5·32	·9866	8·06
·9988	0·64	·9947	2·91	·9906	5·39	·9865	8·13
·9987	0·69	·9946	2·97	·9905	5·45	·9864	8·20
·9986	0·74	·9945	3·02	·9904	5·51	·9863	8·27
·9985	0·80	·9944	3·08	·9903	5·58	·9862	8·34
·9984	0·85	·9943	3·14	·9902	5·64	·9861	8·41
·9983	0·91	·9942	3·20	·9901	5·70	·9860	8·48
·9982	0·96	·9941	3·26	·9900	5·77	·9859	8·55
·9981	1·02	·9940	3·32	·9899	5·83	·9858	8·62
·9980	1·07	·9939	3·37	·9898	5·89	·9857	8·70
·9979	1·12	·9938	3·43	·9897	5·96	·9856	8·77
·9978	1·18	·9937	3·49	·9896	6·02	·9855	8·84
·9977	1·23	·9936	3·55	·9895	6·09	·9854	8·91
·9976	1·29	·9935	3·61	·9894	6·15	·9853	8·98
·9975	1·34	·9934	3·67	·9893	6·22	·9852	9·05
·9974	1·40	·9933	3·73	·9892	6·29	·9851	9·12
·9973	1·45	·9932	3·78	·9891	6·35	·9850	9·20
·9972	1·51	·9931	3·84	·9890	6·42	·9849	9·27
·9971	1·56	·9930	3·90	·9889	6·49	·9848	9·34
·9970	1·61	·9929	3·96	·9888	6·55	·9847	9·41
·9969	1·67	·9928	4·02	·9887	6·62	·9846	9·49
·9968	1·73	·9927	4·08	·9886	6·69	·9845	9·56
·9967	1·78	·9926	4·14	·9885	6·75	·9844	9·63
·9966	1·83	·9925	4·20	·9884	6·82	·9843	9·70
·9965	1·89	·9924	4·27	·9883	6·89	·9842	9·78
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·9962	2·05	·9921	4·45	·9880	7·09	·9839	9·99
·9961	2·11	·9920	4·51	·9879	7·16	·9838	10·07
·9960	2·17	·9919	4·57	·9878	7·23		

The absolute alcohol, with which the experiments which furnished the data for the above Table were made, was prepared as follows:—Carbonate of potassa was exposed to

* 'Memoirs of the Chemical Society,' vol. iii. p. 454.

a red-heat to deprive it of water; and, when sufficiently cool, was pulverized and added to ordinary alcohol of specific gravity ·850 at 60° F. till it ceased to dissolve any more: the whole was then allowed to digest 24 hours, being frequently agitated, when the alcohol was carefully poured off. As much fresh-burned quicklime as was considered sufficient, when powdered, to absorb the whole of the alcohol, was introduced into a retort, and the alcohol added to it; after digesting 48 hours, it was slowly distilled in a water-bath at a temperature of about 180° F. The alcohol thus obtained was carefully redistilled, and its specific gravity at 60° F. was found in two experiments to be ·7946 and ·7947. It was subsequently digested a second and a third time for several days with recently ignited quicklime, and redistilled at 172° F. The mean of several determinations gave the number ·79381, which the author thinks may be regarded as expressing the true specific gravity of absolute alcohol at 60° F.

TABLE XI.—*Tension of Aqueous Vapour at different Temperatures.*

Temperature in degrees (Centigrade).	Tension of the aqueous vapour expressed in millimètres.	Temperature in degrees (Centigrade).	Tension of the aqueous vapour expressed in millimètres.	Temperature in degrees (Centigrade).	Tension of the aqueous vapour expressed in millimètres.
0	4·525	14	11·882	28	28·148
1	4·867	15	12·677	29	29·832
2	5·231	16	13·519	30	31·602
3	5·619	17	14·409	31	33·464
4	6·032	18	15·351	32	35·419
5	6·471	19	16·345	33	37·473
6	6·939	20	17·396	34	39·630
7	7·436	21	18·505	35	41·893
8	7·964	22	19·675	36	44·268
9	8·525	23	20·909	37	46·758
10	9·126	24	22·211	38	49·368
11	9·751	25	23·582	39	52·102
12	10·421	26	25·026	40	54·969
13	11·130	27	26·547		

INDEX.

THE END.

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